BIOMASS PYROLYSIS PROCESSES: PERFORMANCE PARAMETERS AND THEIR INFLUENCE ON BIOCHAR SYSTEM BENEFITS

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A dissertation presented for the degree of Master of Science
University of Edinburgh, 2009

Abstract

This study focuses on performance of biomass pyrolysis processes for use in biochar systems. Objectives are to understand the range of control of such processes and how this affects potential benefits of pyrolysis biochar systems, in particular for climate change mitigation.

Slow, intermediate and fast pyrolysis processes are reviewed. Product yield distributions change depending on feedstock composition and preparation, control of temperature and material flows. These allow some control over distribution of main products – char, liquids and gases. Typical yield ranges for pyrolysis processes are defined. Variability associated with char yield is estimated at ±5% (relative). Char yield should be considered an underlying, but minor source of variability in pyrolysis biochar systems. A model study is used to compare effects on greenhouse gas balance and electricity generating capability of slow, intermediate and fast pyrolysis processes with direct combustion; there is a trade-off between these benefits following from the different product yield distributions. High char yields allow greater net CO2 benefits but lower electrical output from slow or intermediate pyrolysis. Higher liquid and/or gas yields allow greater electrical output from fast pyrolysis but less than from direct combustion. Fast pyrolysis and direct combustion have similar net CO2 effects when retained char is low. If the objectives of pyrolysis biochar systems are for climate change mitigation then processes with higher char yields should be preferred.

The model is sensitive to the reference case chosen for fossil fuel substitution and to the stability of biochar-carbon in soils – a major uncertainty in the analysis of pyrolysis biochar systems. Financial analysis shows the trend in income value for pyrolysis and combustion processes is opposite to the trend in climate change mitigation benefits. Lifecycle CO2 analysis suggests dominant factors in pyrolysis biochar systems relate to carbon sequestration in biochar and fossil fuels substitution by renewable electricity.

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Acknowledgements

I would like to thank staff and students of the UK Biochar Research Centre for their help, advice and useful discussions throughout my dissertation project; in particular my supervisor, Dr Ondřej Masek, for much helpful guidance and Dr Simon Shackley for initially suggesting the topic. I am very grateful to Jim Hammond for providing data from his life-cycle analysis of biochar systems for use alongside my model study.

I also want to thank my family, especially my wife Heather, for their patience and tolerance throughout this year and in particular over the last few weeks; I could not have done this without their support.

Biomass Pyrolysis Processes: Performance Parameters and their Influence on Biochar System Benefits

1 Introduction

1.1 Pyrolysis Biochar Systems: Context

Climate change caused by anthropogenic greenhouse gas emissions is considered by many to be a significant challenge to human civilisation. Much activity is currently focussed on avoiding greenhouse gas emissions through reduction in use of fossil fuels, capturing carbon dioxide emitted from fossil fuel combustion and through changes in land-use and agricultural practices. International achievement in reducing emissions has been limited to date and the global rate of emission continues to increase (Canadell et al, 2007). There is a growing realisation that measures to reduce emissions may prove insufficient to stabilise atmospheric greenhouse gases at levels avoiding dangerous climate change. Hence ways to remove carbon dioxide from the atmosphere are of increasing interest (Lenton and Vaughan, 2009). One such potential measure is the sequestration of carbon in soils in an inert form through pyrolysis biochar systems.

Pyrolysis is a thermo-chemical process in which organic material is converted into a carbon-rich solid (char) and volatile matter (liquids and gases) by heating in the absence of oxygen (Demirbas and Arin, 2002). Char from biomass, termed biochar in this context, when produced and incorporated into soils under certain conditions may be stable over a long timescale. Through such a pyrolysis biochar system carbon dioxide may be removed from the atmosphere, assimilated firstly by plant growth, then stored in a stable soil-carbon pool rather than returning to the atmosphere through decomposition.

As well as this direct 'carbon-negative' potential of pyrolysis biochar systems there are three further related areas of benefit proposed (Lehmann and Joseph, 2009). Addition of biochar to soils can enhance fertility leading to increased crop yields or allowing reduced application of energy-intensive agrochemicals. Liquid and gas co-products of biomass pyrolysis can be used for electricity generation or other fuel use (as well as being used to power the process) thereby offsetting fossil fuel consumption and so avoiding greenhouse gas emissions. Pyrolysis can

also be used to treat biodegradable wastes converting some carbon in them to a stable form and so avoiding greenhouse gas emissions from decomposition. It is the potential for multiple benefits arising simultaneously from pyrolysis biochar systems and having an overall effect of reducing the level of greenhouse gases in the atmosphere that has led recently to rapidly increasing interest in the area.

Estimates of the potential for carbon sequestration using biochar are limited but suggest that the total global scale could be large, possibly on the gigatonne scale, with one suggesting sequestration potential could exceed existing emissions from fossil fuels (Lehmann et al, 2006). Such global estimates are necessarily based on numerous assumptions and are open to criticism. It has been suggested that the efficiency of biochar systems will be strongly dependent on case-specific factors and that it is difficult to assess the overall potential without much further study (Fowles, 2007).

In two recent publications aiming to quantify potential benefits of specific biochar systems (Gaunt and Lehmann, 2008; McCarl et al, 2009) it is notable that the performance parameters of the pyrolysis processes themselves were not considered as variables for sensitivity analysis and essentially single sets of data for the pyrolysis processes have been used. This is a surprising limitation as the pyrolysis process performance is likely to be one of the key factors affecting the efficiency of a pyrolysis biochar system. This limitation spurred the objectives of the present study which aims to investigate the influence of the parameters of pyrolysis processes on benefits arising from biochar systems, focussing on the aspects of energy and carbon balance.

1.2 Benefits and Concerns: Sustainability Issues

There are four main areas, overlapping and interlinked, where the adoption of pyrolysis and biochar systems may bring benefits; these are agricultural soil improvement, waste management, renewable energy production and climate change mitigation (Lehman and Joseph, 2009). Theses are introduced briefly below together with some of the areas of concern raised, including consideration of some associated issues of environmental sustainability.

The use of biochar as a soil improver in agriculture may enhance crop yield through a number of mechanisms including increased nutrient and moisture retention, improved soil structure and increased microbial activity, particularly when applied to poor or degraded soils (Blackwell et al, 2009). This is important in the face of rising food demand with increasing

world population and widespread degradation of soils under existing agricultural practices. Use of biochar for agriculture in developing countries is seen by supporters as a more appropriate approach than that of the Green Revolution. Biochar pyrolysis systems using low entry cost technology can allow sustainable use of existing local resources, such as agricultural residues and fresh biomass, to deliver benefits in soil fertility and the efficient use of applied fertilizers while still providing an energy product (Lehmann and Joseph, 2009). Biochar application may also reduce the release of nitrous oxide from agricultural land.

However, there are many uncertainties surrounding the use of biochar in agriculture. Reported benefits vary with factors such as location, soil type, climate, species of plant studied, the original biomass and the pyrolysis conditions used (Blackwell et al, 2009). This makes the benefits of biochar to agriculture difficult to predict while being key to the adoption of biochar systems. This area is the subject of much ongoing research beyond the scope of this report.

Many organic waste materials can give rise to greenhouse gas emissions on disposal or when left to decompose. Materials including forestry and agricultural wastes, animal wastes, sewage sludge, organic components of municipal solid waste or papermaking and other industrial wastes can all lead to such emissions. Mechanisms include release of methane from landfill, nitrous oxide from inappropriate use of wastes on agricultural land, as well as release of carbon dioxide from natural decomposition or open combustion. Use of pyrolysis to treat these wastes can avoid the methane and nitrous oxide emissions and lock some carbon in a stable form in biochar while the remainder may be used for its energy value as described below. Pyrolysis can also benefit by reducing waste volumes for disposal or transport if equipment is sited near sources (Lehmann and Joseph, 2009)

Pyrolysis processes can be used as part of renewable energy systems based on biomass in a number of ways. Such systems can offset use of fossil fuels and so avoid associated emissions of greenhouse gases. Biomass can simply be burnt to raise steam and so generate electricity and usable heat, but by incorporating a pyrolysis step greater efficiencies and value can potentially be achieved. Efficiencies of biomass energy conversion to electricity by direct combustion are of the order 25-30%; however, by using a pyrolysis-gasification process (converting biomass to syngas) and combined-cycle gas turbine technology the conversion efficiency may be increased to 35-40% (Thornley et al, 2009). Pyrolysis of biomass leads to

liquid and gas products that can be used directly for electricity generation (discussed further in main report sections). The liquid can be upgraded to produce high value products suitable for use as transport fuels (Dynamotive, 2009). Pyrolysis can also be used in combination with a steam reforming step to produce hydrogen for fuel use (Day et al, 2005). In some of these uses a benefit also arises from concentration of energy value into a lower volume product, reducing transport emissions and costs if conversion facilities are appropriately sited.

Char produced by pyrolysis can be used as a renewable fuel. It can be used directly or co-fired with other solid fuels in conventional generating plant. In its traditional form as charcoal it is used extensively for cooking particularly in Africa and other developing regions. Traditional charcoal making processes are often inefficient and are seen as a major source of environmental degradation through deforestation and pollution in rural areas (Kammen and Lew, 2005). Use of pyrolysis technology at appropriate scales in developing countries may be a way to improve efficiencies and sustainability, reducing biomass requirement for the same charcoal output and allowing use of agricultural wastes as alternative feedstock to wood (Pro-Natura, 2008) with the potential for co-products to provide electrical power also. In such processes any retention of char for agricultural use will reduce the energy product available from pyrolysis and so reduce the fossil fuel offset, but this will be balanced by the long-term retention of carbon in the soils as biochar. Emissions of carbon dioxide from burning biomass or pyrolysis products are generally considered as carbon neutral as the carbon has been fixed from the atmosphere in recent times and would return to the atmosphere through decomposition processes if not combusted.

The three areas above each contribute to the fourth area of benefit, that of climate change mitigation. The use of pyrolysis biochar systems may reduce the anthropogenic emission of greenhouse gases to the atmosphere through avoiding release from agriculture, waste disposal or the combustion of fossil fuel. But the most potent benefit may be from the sequestration of carbon by fixing it from the atmosphere in a stable form as biochar, having the effect of reducing levels of carbon dioxide in the atmosphere. These two effects – the avoidance of greenhouse gas emissions and the fixing of atmospheric carbon dioxide in a stable form of carbon – between them represent the climate change mitigation potential of pyrolysis biochar systems.

The way in which biochar is used or stored is, in a sense, secondary to the effect of fixing carbon from the atmosphere. The use in agriculture is seen as the most promising possibility for the synergistic reasons discussed above, but to be effective it depends on the lifetime of biochar-carbon in soils being significantly longer than the decomposition rate of biomass. This is an area of uncertainty discussed later in the report (Section 5.8.2). Other possibilities for carbon sequestration as char have been suggested, such as simple burial in abandoned mines or as artificial marine sediments (Lovelock, 2009), however, these remain at the level of conjecture.

One of the main concerns about pyrolysis biochar systems centres on the risk that if it is made financially attractive through use of subsidy, it will spur large scale plantations of crop specifically for biochar with the same negative effects as have been experienced with other bio-fuel developments: effects on food prices, replacement of existing natural ecosystems by mono-cultural plantations, consequent effects of biodiversity and indigenous people, loss of existing soil carbon from preparation for plantations (Monbiot, 2009). Proponents of biochar usually emphasise the use of current waste materials as feedstocks for pyrolysis or the cultivation of specific fuel crops on land otherwise not suitable for food production (Lehmann et al, 2006).

The diversity of viewpoints on pyrolysis biochar systems reflects the fact that the area is relatively under-researched and many uncertainties remain. One area of uncertainty is how the performance of pyrolysis processes affects the combination of benefits and so how best to specify and operate such processes; this area forms the main subject of the present study.

1.3 Study Objectives

The project has two principal objectives.

Firstly, it aims to provide an assessment of the range of control and variability of pyrolysis processes for the treatment of biomass. To achieve this an assessment is made of the scope for intentional variation of process outputs – the yields and properties of products – by choice of technique, equipment or operating conditions for a given feedstock and the influence of feedstock choice. The likely scale of unintentional variation in process outputs is also examined and the effect this may have on predicted outcomes of pyrolysis biochar systems is considered.

The second main objective is to understand how this range of control of pyrolysis may affect the overall energy and carbon balance of pyrolysis biochar systems, and so affect their benefit to climate change mitigation. This is considered primarily within a limited boundary comprising the pyrolysis process, sequestration of carbon in biochar and conversion of products to electrical energy. Specific practical pyrolysis examples are compared and a model is used to estimate the benefits for climate change mitigation and for electrical output. Brief consideration of issues outside the model boundaries is made covering financial aspects, the effect of biochar stability and whole life-cycle assessment.

1.4 Structure of Report

The report is structured in four main sections. Sections 2 to 4 address the first main project objective of understanding the range of control and variability of pyrolysis processes for the treatment of biomass.

Section 2, provides an introduction to biomass pyrolysis covering the main types of process and equipment with some historical context. The main controllable process parameters and their effects on product yields and compositions are discussed. The key effect of biomass feedstock composition is described. Material flows, focussing on carbon, and energy flows of the different types of process are described qualitatively.

Following this, Section 3 describes a review of individual pyrolysis processes with a number of different feedstocks where published data is available. The overall range of potential performance is explored and a view of typical performance is given for main process types and feedstocks.

Section 4 focuses on the unintentional variability of these processes, specifically the variability in product yields. Limited evidence of variability is presented and the significance of this in some literature case studies of biochar systems is discussed.

Section 5 tackles the second project objective. Using published and derived data for selected pyrolysis processes a spreadsheet model is used to investigate the carbon and energy flows. Methodology and data for the process examples and reference cases are described. The relative benefits of the process examples towards climate change mitigation and their potential electrical outputs are compared. Sensitivity to some key model assumptions is tested and a limited comparison with literature benchmarks is made. The model is used to explore

scenarios across the range of control of the main pyrolysis types. Some pointers toward the best way of achieving benefits within the model scope are suggested. Finally the model is related to reality by considering three areas beyond the model boundary. A simple financial analysis is made. Uncertainties over stability of biochar in soils and the effect on biochar system benefits are discussed. Greenhouse gas effects upstream and downstream of the model boundaries are considered to give a whole life-cycle assessment for selected examples of pyrolysis biochar systems. For this last point data on upstream and downstream effects was kindly provided by Jim Hammond (2009) from his MSc dissertation work.

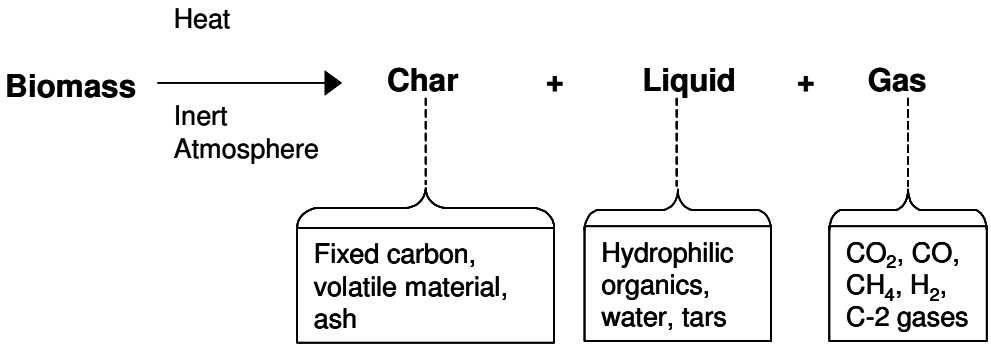
Conclusions of the study are summarised in a final section where some recommendations for future research directions in pyrolysis technology and some thoughts on experimental protocols are also collected.

2 Biomass Pyrolysis Processes

2.1 Introduction

2.1.1 Definition

Pyrolysis is a thermo-chemical decomposition process in which organic material is converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen (Demirbas and Arin, 2002). The solid, termed variously as char, biochar, charcoal or coke, is generally of high carbon content and may contain around half the total carbon of the original organic matter. The volatiles can be partly condensed to give a liquid fraction leaving a mixture of so-called 'non-condensable' gases. The process is represented simply in Equation 1. Each of the three product streams from pyrolysis, solid, liquid and gas, can have properties and uses that provide value from the process.



Equation 1. Simple Representation of Pyrolysis Process

2.1.2 Product Terminology

In this report the term char will be used generally to describe the solid product of pyrolysis, charcoal will be used for more traditional processes with wood as feedstock, biochar will be used where the intention is for the char to be used as a soil amendment. The term coke will not be used here being more generally used for coal-derived char. Char contains a varying carbon content, typically ranging 60-90% (Gaur and Reed, 1995). Some is 'fixed-carbon' in terms of its proximate analysis, some present in a remaining volatile portion; inorganic material in char is termed ash.

Liquid products from biomass pyrolysis are frequently termed bio-oil. However, this is a somewhat confusing term as the organic liquid product is generally hydrophilic containing many oxygenated compounds and is present, sometimes as a single aqueous phase, sometimes phase-separated, together with water produced in the pyrolysis reaction or remaining from the feedstock (Demirbas and Arin, 2002). In this report this is generally referred to simply as the liquid product and includes the water unless otherwise stated.

The gas product is termed synthesis gas, shortened to syngas. It is generally composed of carbon dioxide, carbon monoxide, methane, hydrogen and two-carbon hydrocarbons in varying proportions. In this report it is often referred to simply as the gas product.

2.1.3 Historical Context

Mankind has used pyrolysis and related processes for thousands of years. The earliest known example is the use of charcoal, produced as an unintentional residue from cooking fires, for cave drawings by Cro-Magnon man some 38,000 years ago (Antal and Grønli, 2003). In the Bronze Age intentionally produced charcoal was used for smelting metals and charcoal is still heavily used in metallurgy today. For thousands of years charcoal has been a preferred cooking fuel. Prior to the development of petrochemicals, pyrolysis, or 'wood distillation', was a source of many valuable organic compounds for industrial and medicinal uses; some high value liquid products, such as flavourings, are still produced by wood pyrolysis (Bridgwater and Peacocke, 2000). Pyrolysis and gasification processes have been used to extract liquid and gas products from coal since Victorian times and the technology for producing a synthetic crude oil from coal is well established. It is only more recently that biomass and organic wastes have become a focus as feeds for pyrolysis and related thermal treatment processes for energy recovery or bio-fuel production; the technologies are still relatively undeveloped (Mistry et al, 2008).

Char has also been used in agriculture for thousands of years. The fertile *terra preta* (dark earth) soils of the Amazonian region result from incorporation of char into otherwise poor soils. The resulting soils have long-lasting fertility that has been related to the stability of carbon in the soil (Lehmann et al, 2009). It is this observation coupled with the search for carbon sequestration techniques for climate change mitigation that has led to recent interest in pyrolysis-derived char, or biochar.

2.2 Pyrolysis Process Types

There are two main classes of process for biomass pyrolysis, introduced briefly below, plus a number of other related technologies. These sections are intended to give an overview of the technologies only; references to detailed published reviews are given. More detail on selected technologies, used in modelling work for this study, is given later in Section 5.3.

2.2.1 Fast Pyrolysis

Fast pyrolysis is characterised by high heating rates and short vapour residence times. This generally requires a feedstock prepared as small particle sizes and a design that removes the vapours quickly from the presence of the hot solids. There are a number of different reactor configurations that can achieve this including ablative systems, fluidised beds, stirred or moving beds and vacuum pyrolysis systems. A moderate (in pyrolysis terms) temperature of around 500°C is usually used. Development of fast pyrolysis progressed rapidly following the oil crises of the 1970's as a way of producing liquid fuel from an indigenous renewable resource, primarily wood, and the process is designed to give a high yield of bio-oil. There are several well-established commercial processes such as Ensyn Corporation's Rapid Thermal Process (Ensyn, 2009) or Dynamotive's Biotherm process (Dynamotive, 2009). The area has been extensively reviewed by Bridgwater (e.g. Bridgwater et al, 1999; Bridgwater and Peacocke, 2000).

2.2.2 Slow Pyrolysis

Slow pyrolysis can be divided into traditional charcoal making and more modern processes. It is characterised by slower heating rates, relatively long solid and vapour residence times and usually a lower temperature than fast pyrolysis, typically 400°C. The target product is often the char, but this will always be accompanied by liquid and gas products although these are not always recovered.

Traditional processes, using pits, mounds or kilns, generally involve some direct combustion of the biomass, usually wood, as heat source in the kiln. Liquid and gas products are often not collected but escape as smoke with consequent environmental issues. Developments through the late 19^{th} and early 20^{th} centuries led to industrial scale processes using large retorts operated in batch (e.g. Riechert process, VMR ovens) or continuous modes (e.g. Lambiotte process). These allow recovery of organic liquid products and recirculation of gases to provide process heat, either internally or externally (Antal and Grønli, 2003). Prior to the widespread availability of petrochemicals, such processes were used to generate important

organic liquid products, in particular acetic acid and methanol. An excellent review of the science behind charcoal making is given by Antal and Grønli (2003).

Other developments in the later 20th century led to slow pyrolysis technologies of most interest for biochar production. These are generally based on a horizontal tubular kiln where the biomass is moved at a controlled rate through the kiln; these include agitated drum kilns, rotary kilns and screw pyrolysers (Brown, 2009). In several cases these have been adapted for biomass pyrolysis from original uses such as the coking of coal with production of 'towns gas' or the extraction of hydrocarbons from oil shale (e.g. Lurgi twin-screw pyrolyser, Henrich, 2007). Although some of these technologies have well-established commercial applications, there is as yet little commercial use with biomass in biochar production. Examples in this context include BEST Energies' process using an agitated drum kiln (BEST Energies, 2009; Downie et al, 2007) and Pro-Natura's Pyro-6 and Pyro-7 technology (Pro-Natura, 2008). No comprehensive review of modern slow pyrolysis techniques is available, however, Brown (2009) summarises them briefly together with other potential techniques for biochar production.

2.2.3 Other Technologies

This section covers a brief review of technologies other than slow and fast pyrolysis that may be used for thermal treatment of biomass and char production. Other than the first mentioned, they are not considered further in this report.

The term 'intermediate pyrolysis' has been used to describe biomass pyrolysis in a certain type of commercial screw-pyrolyser – the Haloclean reactor (Hornung, 2004, Hornung et al, 2006). This reactor was designed for waste disposal of electrical and electronic component residues by pyrolysis. When used for biomass it has performance similar to slow pyrolysis techniques, although somewhat quicker. The Haloclean process is modelled in the current study and is described more fully in Section 5.3.2. Other than this application the term intermediate pyrolysis has been used occasionally but not consistently in the literature.

Very fast pyrolysis is sometimes referred to as 'flash pyrolysis' (Demirbas and Arin, 2002), usually in the context of laboratory studies involving rapid movement of substrate through a heated tube under gravity or in a gas flow. Higher temperatures and shorter residence times than fast pyrolysis are used, the main product distributions are similar to fast pyrolysis.

Flash carbonisation is a different process involving partial combustion of a packed bed of biomass in a pressurised reactor with a controlled air supply. A high yield of char and gas are reported with no liquid product formed under the reaction conditions (Antal et al, 2003). The technology is currently being commercialised by Carbon Diversion Incorporated (CDI, 2009).

Gasification is an alternative thermo-chemical conversion technology suitable for treatment of biomass or other organic matter including municipal solid wastes or hydrocarbons such as coal. It involves partial combustion of biomass in a gas flow containing a controlled level of oxygen at relatively high temperatures (500-800°C) yielding a main product of combustible syngas with some char. Although designed to produce gas, under some conditions gasifiers can produce reasonable yields of char and have been proposed as an alternative production route to pyrolysis for biochar (Brown, 2009).

Hydrothermal carbonisation is a completely different process involving the conversion of carbohydrate components of biomass (from cellulose) into carbon-rich solids in water at elevated temperature and pressure (Titirici et al, 2007). Under acidic conditions with catalysis by iron salts the reaction temperature may be as low as 200°. The process may be suitable for concentration of carbon from wet waste streams that would otherwise require drying before pyrolysis, making it complementary to pyrolysis and a potential alternative to anaerobic digestion for treatment of some wastes.

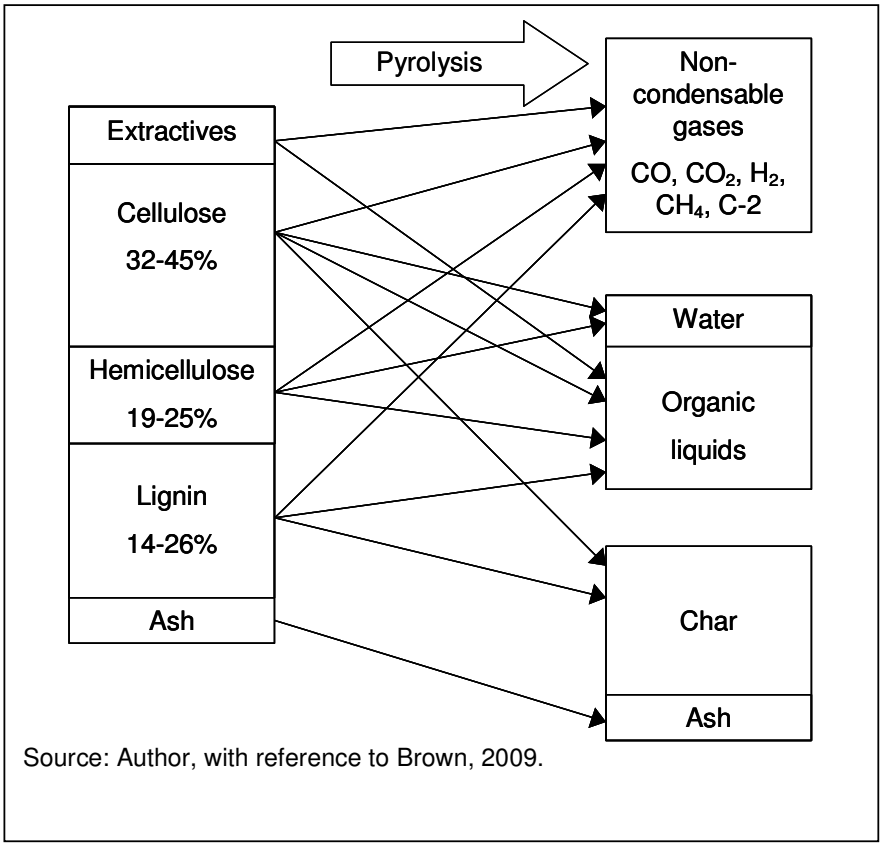
2.3 Effects of Feedstock and Main Process Parameters

This section describes the effect of the main controllable factors affecting the distribution of products from pyrolysis processes. The effect of feedstock composition and preparation is discussed first followed by the effects of process operating conditions. Slow, intermediate and fast pyrolysis are all affected in a related manner but the importance of factors and the effect of changes on product yield distribution differs between process types.

2.3.1 Feedstock Composition

Biomass is generally composed of three main groups of natural polymeric materials: cellulose, hemicellulose and lignin. Other typical components are grouped as ‘extractives’ (generally smaller organic molecules or polymers) and minerals (inorganic compounds). These are present in differing proportions in different biomass types and these proportions influence the product distributions on pyrolysis (Antal and Grønli, 2003; Brown, 2009; Mohan et al, 2006).

On heating to pyrolysis temperatures the main components contribute to product yields broadly as follows (Antal and Grønli, 2003). Primary products of hemicellulose and cellulose decomposition are condensable vapours (hence liquid products) and gas. Lignin decomposes to liquid, gas and solid char products. Extractives contribute to liquid and gas products either through simple volatilisation or decomposition. Minerals in general remain in the char where they are termed ash. This distribution of components into products is shown schematically in Figure 1.



Source: Author, with reference to Brown, 2009.

Figure 1. Simplified Representation of Biomass Pyrolysis

Vapours formed by primary decomposition of biomass components can be involved in secondary reactions in the gas phase, forming soot, or at hot surfaces, especially hot char surfaces where a secondary char is formed (Antal and Grønli, 2003). This is particularly

important in understanding the differences between slow and fast pyrolysis and the factors affecting char yields and is discussed further in Section 2.3.4 below.

Minerals in biomass, particularly the alkali metals, can have a catalytic effect on pyrolysis reactions leading to increased char yields in some circumstances, in addition to the effect of ash contributing directly to char yield. Minerals also affect the reactivity and ignition properties of chars (Antal and Grønli, 2003).

2.3.2 Feedstock Preparation

Moisture content can have different effects on pyrolysis product yields depending on the conditions (Antal and Grønli, 2003). In traditional charcoal kilns heated internally by wood combustion, high moisture levels lead to reduced charcoal yields as a greater quantity of wood must be burnt to dry and heat the feed. For externally heated equipment the reported effect of steam on the yield of char varies depending on the conditions. Increased moisture present when pyrolysis reactions are performed under pressure has been shown to systematically increase char yields (Antal and Grønli, 2003).

Fast pyrolysis processes in general require a fairly dry feed, around 10% moisture (Bridgwater and Peacocke, 2000), so that the rate of temperature rise is not restricted by evaporation of water. Slow pyrolysis processes are more tolerant of moisture, the main issue being the effect on process energy requirement. For charcoal making, wood moisture contents of 15-20% are typical (Antal and Grønli, 2003). In all pyrolysis processes water is also a product and is usually collected together with other condensable vapours in the liquid product. Moisture in the reaction affects char properties and this has been used to produce activated carbons through pyrolysis of biomass (Zanzi et al, 2001).

Feed particle size can significantly affect the balance between char and liquid yields. Larger particle sizes tend to give more char by restricting the rate of disengagement of primary vapour products from the hot char particles, so increasing the scope for secondary char-forming reactions (discussed further in Section 2.3.4) (Antal and Grønli, 2003). Hence larger particles are beneficial in processes targeting char production and small particles are preferred to maximise liquid yields in fast pyrolysis.

2.3.3 Temperature Profile Control

The temperature profile is the most important aspect of operational control for pyrolysis processes. Material flow rates, both solid and gas phase, together with the reactor temperature control the key parameters of heating rate, peak temperature, residence time of solids and contact time between solid and gas phases. These factors affect the product distribution and the product properties.

For fast pyrolysis a rapid heating rate and a rapid rate for cooling primary vapours are required to minimise the extent of secondary reactions. These reactions not only reduce the liquid yield but also tend to reduce its quality, giving a more complex mixture, an increased degree of polymerisation and higher viscosity (Bridgwater and Peacocke, 2000). Conversely, in slow pyrolysis there is some evidence that slow heating leads to higher char yields, but this is not consistent (Antal and Grønli, 2003).

Peak temperature, however, has an unequivocal effect on char yields and properties. Higher temperatures lead to lower char yield in all pyrolysis reactions. This results from the main controlling variable of pyrolysis reaction kinetics being temperature (Antal and Grønli, 2003). The effect can be thought of as more volatile material being forced out of the char at higher temperatures reducing yield but increasing the proportion of carbon in the char. Temperature also has an effect on char composition, chars produced at higher temperatures having higher carbon contents both total- and fixed-carbon (Antal and Grønli, 2003). This may have important implications for biochar stability in soils and is discussed in detail in Section 5.8.2 below. Solid residence time is also important but to a lesser degree than peak temperature, longer time at temperature leading to lower char yield (Antal and Grønli, 2003).

The effect of temperature on liquid and gas yields is more complex. Liquid yields are higher with increased pyrolysis temperatures up to a maximum value, usually at 400-550°C but dependent on equipment and other conditions. Above this temperature secondary reactions causing vapour decomposition become more dominant and the condensed liquid yields are reduced. Gas yields are generally low with irregular dependency on temperature below the peak temperature for liquid yield; above this gas yields are increased strongly by higher temperatures, as the main products of vapour decomposition are gases. For fast pyrolysis the peak liquid yields are generally obtained at a temperature of around 500°C (Bridgwater et al, 1999). Peak liquid yields for slow pyrolysis are more variable. Demirbas (2001) reports peak

liquid yields of 28-41% at temperatures between 377°C and 577°C, depending on feedstock, when using a laboratory slow pyrolysis technique. The Haloclean process yields a peak of 42-45% liquid at temperatures of 385-400° with different straw feeds (Hornung et al, 2006).

The effects of peak pyrolysis temperature are shown for fast and intermediate pyrolysis examples in Figure 2; the trends for typical slow pyrolysis processes are similar to intermediate pyrolysis.

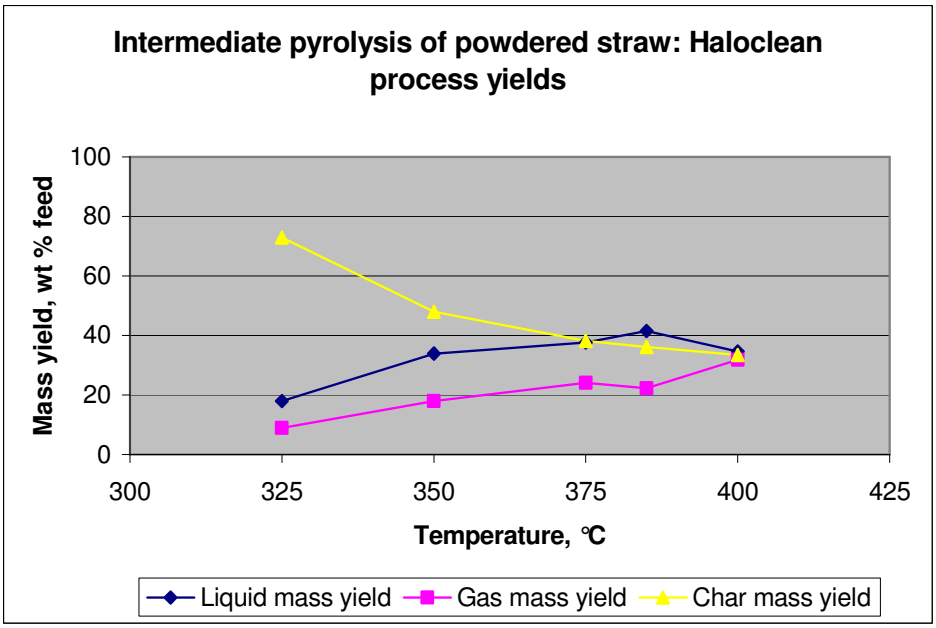
2.3.4 Gas Environment

Conditions in the gas phase during pyrolysis have a profound influence on product distributions and on the thermodynamics of the reaction. Most of the effects can be understood by considering the secondary char-forming reactions between primary vapour products and hot-char. The area is discussed in detail and rationalised by Antal and Grønli (2003) in the context of charcoal making; the main points are summarised here.

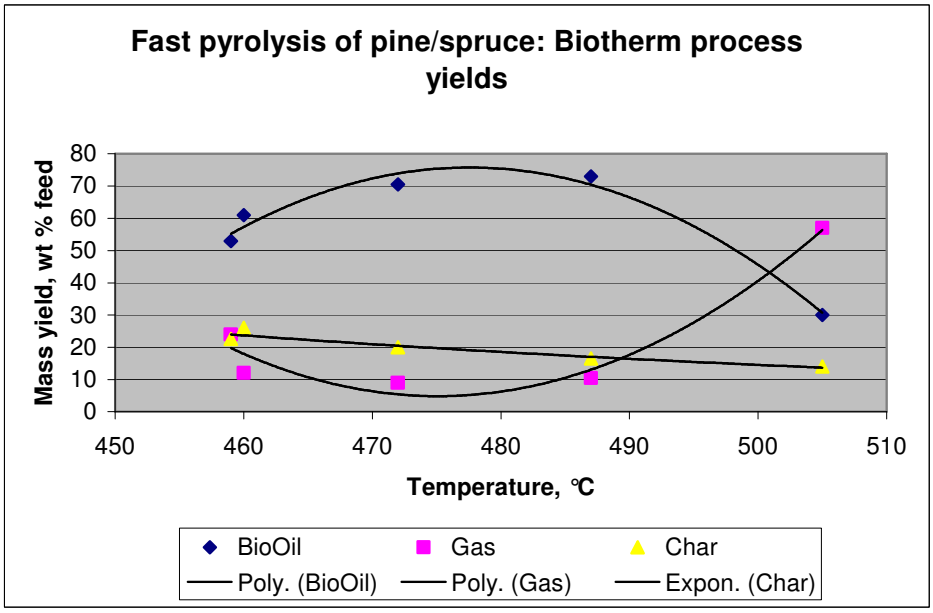
Gas flow rate through the reactor affects the contact time between primary vapours and hot char and so affects the degree of secondary char formation. Low flows favour char yield and are preferred for slow pyrolysis; high gas flows are used in fast pyrolysis, effectively stripping off the vapours as soon as they are formed.

Pressure has a similar effect. Higher pressure increases the activity of vapours within and at the surfaces of char particles so increasing secondary char formation. The effect is most marked at pressures up to 0.5MPa. Conversely, pyrolysis under vacuum gives little char, favouring liquid products. For pyrolysis under pressure, moisture in the vapour phase can systematically increase the yield of char, believed to be due to an autocatalytic effect of water, reducing the activation energy for pyrolysis reactions.

The thermodynamics of pyrolysis are also influenced by gas environment. The reaction is more exothermic at higher pressures and low flow rates. This is rationalised as being due to the greater degree of secondary char-forming reaction occurring. Hence, higher char yields are associated with conditions where pyrolysis is exothermic; such conditions will favour the overall energy balance of processes targeting char as product.



Source: Hornung, 2008.



Source: Dynamotive, 1999

Figure 2. Product Yield Trends with Pyrolysis Temperature

In summary, any factor of pyrolysis conditions that increases the contact between primary vapours and hot char, including high pressure, low gas flow, large particles or slow heating is likely to favour char formation at the expense of liquid yield. Antal and Grønli (2003) provide data from their own work indicating that chars formed under low flow, high pressure conditions with consequent higher char yields also have higher fixed-carbon yields. This effect may be useful in maximising the carbon sequestration potential in biochars although there may be other changes in the char properties that are not immediately evident.

2.4 Carbon and Energy Flows on Pyrolysis

To determine how pyrolysis processes and biochar systems may benefit climate change, through their effect on emissions of greenhouse gases, an understanding of carbon and energy flows is required. This section gives a qualitative description of the main flows and considerations as an introduction to later sections that aim to quantify the effects. A simple scheme showing the main carbon flows associated with biomass pyrolysis is given in Figure 3.

Carbon is drawn from the atmosphere as carbon dioxide by growing plants through photosynthesis and assimilated into biomass. Under natural processes of death and decomposition the carbon is released as carbon dioxide back to the atmosphere in a fairly short timescale. Biomass has an energy value roughly related to its carbon content (together with contributions from other elements and factors). This energy can be released through combustion and used for purposes such as electricity generation or heating. The carbon is thermo-chemically oxidised to carbon dioxide and returns to the atmosphere. In this manner the energy available from biomass is considered renewable and carbon neutral. If the usable energy so produced substitutes energy that would otherwise be obtained by burning fossil fuels, then the carbon dioxide emission associated with the fossil fuel combustion is avoided.

If biomass is pyrolysed, the carbon and the energy value are split between the three product streams: char, liquid and gas. The total mass of the products will be equal to the mass of the starting material, if properly accounted, and the total carbon content of the products will also equal that of the biomass. However, some energy is inevitably lost as heat from the process meaning the total energy value in the products is less than the starting material. Some energy is also required to run the pyrolysis process: to dry the feed, to heat to temperature, to drive equipment. In theory, all this can be supplied by recycle from the products, once the process

has been started-up, with the effect that the product quantities available for use downstream of the pyrolysis process are reduced.

As with the biomass feed, the char and liquid products have energy values roughly related to their carbon contents. Release of this energy by combustion can again be considered as renewable and is largely carbon neutral (some emissions are associated with feedstock production and transport); the carbon returned to the atmosphere as carbon dioxide is the same as would otherwise have resulted from biomass decomposition. If the char product is not burnt, but retained in a way that the carbon in it is stable, then that carbon can be equated to carbon dioxide removed from the atmosphere and sequestered.

The gas product is typically a mixture of carbon dioxide (9-55% by volume), carbon monoxide (16-51%), hydrogen (2-43%), methane (4-11%) and small amounts of higher hydrocarbons (composition ranges from references cited in Appendix 2). The gases are usually present with nitrogen introduced to inert the pyrolysis equipment, this can be treated as a diluent and ignored for material balancing but will affect the heating value of the syngas. The carbon dioxide and nitrogen provide no energy value in combustion, the other gases are flammable and provide energy value in proportion to their individual properties. Again use of the energy in the gas can be considered as renewable and largely carbon neutral. No special consideration of the carbon dioxide in the pyrolysis gas is required as it is not additional to what would result from biomass decomposition.

As with biomass, any usable energy from combustion of the three pyrolysis products that substitutes for fossil fuel use is considered to avoid carbon dioxide emissions.

To summarise, from the point of view of carbon accounting and the effect on carbon dioxide in the atmosphere, carbon flows involved in biomass growth, decomposition and combustion, including the combustion of biomass pyrolysis products, can be considered as carbon neutral, having no effect on atmospheric carbon dioxide. Energy from biomass or its pyrolysis products used to substitute energy from fossil fuels leads to avoidance of carbon dioxide emissions compared to a reference case of fossil fuels use. Carbon stored in char is equated to carbon dioxide removed from the atmosphere. The sum of these last two effects gives the net effect on atmospheric carbon dioxide of biomass pyrolysis processes.

There are clearly important considerations omitted from this simplification, a key one being the stability of carbon in char when used as biochar in soil amendment. The significance of this will be discussed later in Section 5.8.2.

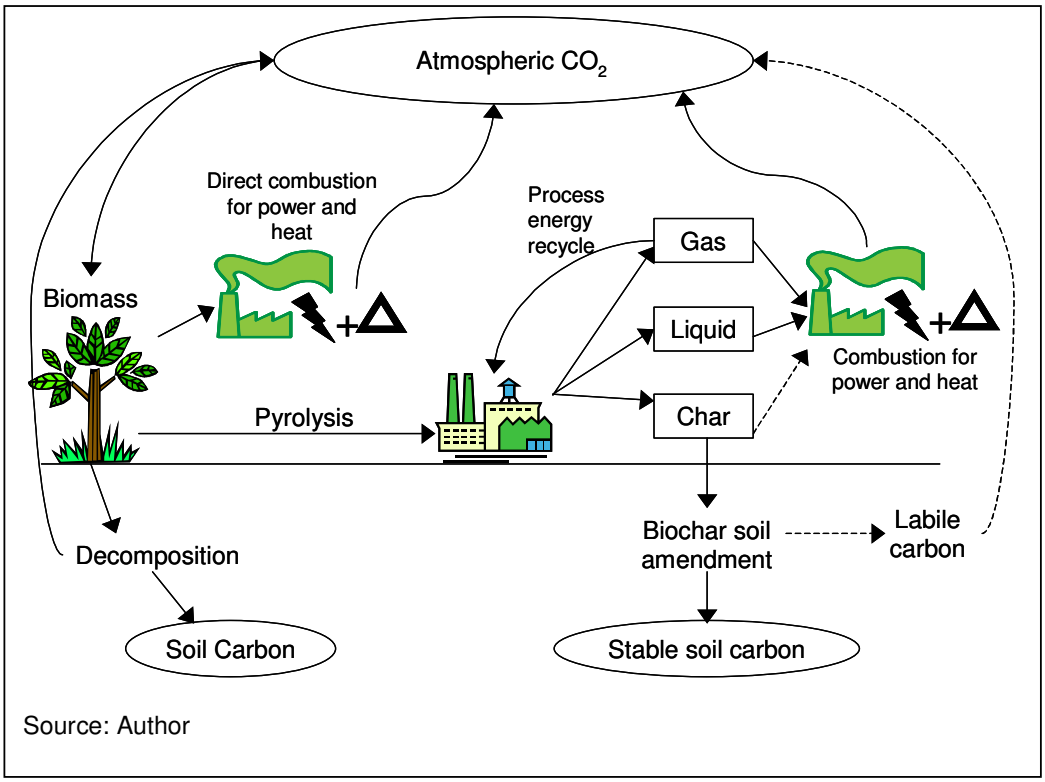


Figure 3. Scheme Showing Main Carbon Flows Associated with Biomass Pyrolysis

3 Biomass Pyrolysis: Review of Process Scope

3.1 Review Methodology

One aim of this study is to understand the scope of biomass pyrolysis processes appropriate for biochar production in terms of their range of feedstock, process and equipment type, operating conditions, product yields and energy values. A review of literature in the field was carried out covering charcoal making, laboratory-scale slow pyrolysis and a small number of reports on pilot or commercial scale 'modern' slow pyrolysis. Fast pyrolysis was covered to a limited extent focusing on pilot or commercial scale and laboratory-scale reports with good yield data. The review covered some sixty items and may be considered indicative but not comprehensive, there is much more published work on laboratory-scale processes and fast pyrolysis in particular. Summary information extracted from the review is given in Appendix 1 and discussed below.

3.2 Observations

There are a number of general observations that can be made on the literature reviewed.

Of the published work on slow pyrolysis most is focused on traditional charcoal making or is based on laboratory-scale studies, there is very little on the recent area of interest in producing biochar with co-products used for energy. The focus on charcoal means there is little available yield data for the liquid and gas co-products and even less where the energy values of the co-products are given. For fast pyrolysis processes, with their focus on conversion to energy products and greater degree of development, data coverage is better, but there are still very few reports giving sufficient data to construct complete energy and carbon balances over the process. Although many reports give a range of yields for varying conditions or feeds, few give data that shows reproducibility of results, a point that is taken up in Section 4.

3.3 Pyrolysis Process Scope

The total scope of pyrolysis processes reviewed, in terms of feedstock, operating conditions and product yields, is very wide. Pyrolysis of scores of different feedstocks has been reported, temperature and residence times varying over a wide range have been used and consequently yields of each of the three products also vary over wide ranges. Yield distributions are specific to individual sets of feed and process variables. However, typical ranges may be

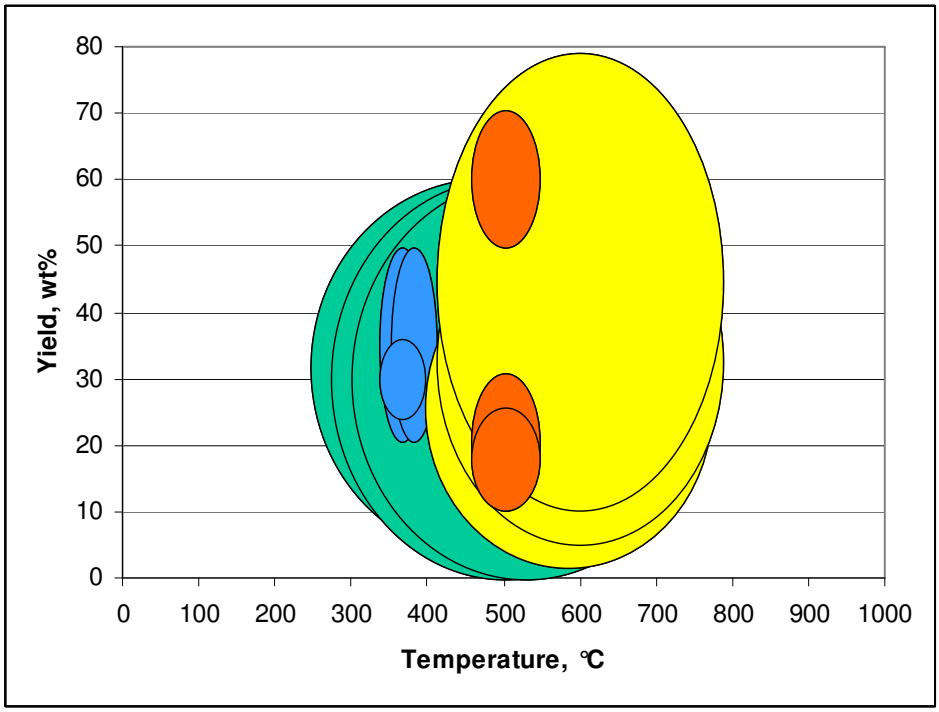
suggested from the review. Table 1 summarises the wider and typical ranges for key variables and product yields. Figure 4 attempts to give an idea of the process envelope in terms of temperature and product yields. It should be noted that the yields are interdependent and will always total 100% if fully accounted.

Table 1. Scope of Pyrolysis Process Control and Yield Ranges

		Slow Pyrolysis	Intermediate Pyrolysis	Fast Pyrolysis
Feed		Scores of feeds reported		
Temperature, ℃	Range	250 - 750	320 - 500	400 - 750
	Typical	350 - 400	350 - 450	450 - 550
Time	Range	mins - days	1 - 15 mins	ms - s
	Typical	2 - 30 mins	4 mins	1 - 5 s
Yields, % wt on dry				
Char	Range	2 - 60	19 - 73	0 - 50
	Typical	25 - 35	30 - 40	10 - 25
Liquid	Range	0 - 60	18 - 60	10 - 80
	Typical	20 - 50	35 - 45	50 - 70
Gas	Range	0 - 60	9 - 32	5 - 60
	Typical	20 - 50	20 - 30	10 - 30

Source: References for literature review, see Appendix 1

Although it is useful to summarise typical ranges of product yields for the main pyrolysis processes there will be many exceptions to these ranges. If comparing different processes or basing conclusions on a process output it is important that the key variables and the feedstock are defined, otherwise it is not possible to know whether conclusions are specific to that example or more generally applicable.



Notes: The three large green ellipses indicate the total scope of operating range reported, in terms of temperature and yields, for the three products of slow pyrolysis, char, liquid and gas. The smaller blue ellipses show the typical ranges for slow pyrolysis, the smallest indicating char yield range for typical temperatures.
Yellow and orange ellipses give the same indications for fast pyrolysis; the higher yield ranges are for liquids.
Intermediate pyrolysis is not shown.
Source: Author.

Figure 4. Pictorial Representation of Pyrolysis Process Scope

3.4 Example Pyrolysis Data

From the first level literature review of pyrolysis processes, reports on processes involving specific feedstocks were selected and more detailed information extracted. The feeds were selected as those most likely to be available for biochar production in the UK in collaboration with a project team studying the potential for biochar pyrolysis systems (Sohi et al, 2009, unpublished work). Selected feeds were spruce wood, miscanthus, wheat straw, willow, and

chicken litter. Full extracted information is included in Appendix 2; a summary of the key data available is given in Table 2.

The data in Table 2 allow a very limited comparison of the effect of different process types on product distributions from the same feedstock, but the consistency of the process examples is poor making paired comparisons difficult. The broad differences and trade-off expected between yields of slow and fast pyrolysis for char and liquid products are evident, although they are confounded by high gas yields in some cases. One exception is the fast pyrolysis of chicken litter where the char yields are high and equal to or greater than the liquid yields; this is explained by very high ash contents in the feed (*ca.*20%) and char (*ca.*40-60%wt) (Kim et al, 2009). The data exemplifies the wide range of yields discussed in the previous section, for instance char yields from slow pyrolysis ranging 12 to 61%. There is very limited data available on energy values of the products, only the set for intermediate pyrolysis of straw allowing a full energy balance calculation.

3.5 Pyrolysis Process Scope: Conclusions

Taken as a whole, this review of pyrolysis process scope shows that for any given feedstock it is possible to vary the product distribution between char, liquid and gas, within limits, by choice of process type and operating conditions. Higher char yields are obtained by slow pyrolysis processes with lower temperatures and low flow rates; higher liquid yields arise from fast pyrolysis processes, specific temperatures and high flow rates. The gas yield is not usually the focus of slow or fast pyrolysis and is generally not actually measured but calculated by difference in mass balance. High gas yields would best be provided by gasification processes, not covered by this review.

Similarly, for any given process and equipment set-up, different product distributions will arise from different feedstocks depending on their composition. However, this should not be a major factor in choice of feedstock for pyrolysis, as controllable operating conditions, such as temperature, generally have a larger effect and could be changed to adjust product distributions. Choice of feedstock is more likely to be dependent on factors such as availability, cost and sustainability considerations.

The wide envelopes of process operation and product distribution for pyrolysis processes imply that choices over process type, operation or feedstock may give different outcomes in

terms of effect on climate change mitigation, or other objectives. This is considered in Section 5.

Table 2. Summary of Pyrolysis Data for Selected Feedstocks

Feed	Process Type and Reference	Feed Moisture	Feed Energy	Pyrolysis Temp-erature	Char Yield	Char Energy	Char Energy Yield	Gas Yield	Gas Energy	Gas Energy Yield	Liquid Yield	Liquid Energy	Liquid Energy Yield
		%wt	MJ/kg	°C	%wt	MJ/kg	% feed energy	%wt	MJ/kg	% feed energy	%wt	MJ/kg	% feed energy
Spruce	Fast pyrolysis, Waterloo process, continuous shallow fluidised bed (Scott et al, 1999)	7		500	12			8			78		
Spruce	Fast pyrolysis, Lurgi-Ruhrgas twin-screw pyrolyser, (Henrich, 2007)	9	16	500	17			13			70		
Spruce	Fast vacuum pyrolysis, Pyrovac process, agitated vacuum tube, (Bridgwater and Peacocke, 2000)	15		450	24			12			64		
Spruce	Slow pyrolysis, laboratory, sealed tube, (Demirbas, 2001)		19.77	377	32.6	29.34	48	20.2			47.2		
Miscanthus	Fast pyrolysis with partial combustion, fluidised bed, (Rocha et al, 2002)	10-12	17.7	450-500	12-15	20-25	17	10-12			70-75		
Miscanthus	Slow pyrolysis, laboratory, rotary kiln, (Michel et al, 2006)	9.6		500	23,28	29		46,51			26		
Miscanthus	Slow pyrolysis with steam activation, laboratory, vertical tube packed bed, (Zanzi et al, 2001)	6.6		550	24			10			66		
Wheat Straw	Fast pyrolysis, Biotherm process, deep fluidised bed, (Scott et al, 1999; Radlein and Kingston, 2007)	1,8		440-550	18-30			18-24			49-58		
Wheat Straw	Intermediate pyrolysis, Haloclean process, rotary kiln with screw, (Hornung et al, 2006)		15.9	400	33-35	25	52-55	20-32	11	14-22	35-45	12	26-34
Wheat Straw pellets	Slow pyrolysis with steam activation, laboratory, vertical tube packed bed, (Zanzi et al, 2001)	6.9		550	25			12			63		
Willow	Slow pyrolysis, laboratory, horrizontal tube with silica, (Leivens et al, 2009)	10,12	16,14	350	61,55			<1			38,45	23	55,74
Willow	Slow pyrolysis with steam activation, laboratory, vertical tube packed bed, (Zanzi et al, 2001)	7.3		650	12			49			39		
Chicken Litter	Fast pyrolysis, bench scale fluidised bed, (Kim et al, 2009; Mante, 2008)	8-10	15	450,470	41,43			36,13			23,43	27,30	41,86

4 Variability in Pyrolysis Processes

4.1 Introduction

The previous section established that the product distributions of pyrolysis processes can fall within a wide envelope and that they can be selected, or controlled to a degree, by choice of feedstock, process type, and operating conditions. In this section the variability associated with a specific set of choices is examined. That is, how reproducible are product distributions for a given combination of process, feedstock and operating conditions? It is important to understand this to know how much credence to put on assessments of biochar systems where a single yield figure is used for char. If there is an inherent variability in char yield the benefits arising from biochar systems can also be expected to be variable. This section considers the sources, evidence and magnitude of yield variability. The sensitivity of system benefits to biochar yield variation in a number of literature case studies is also examined.

4.2 Sources of Variability

Sources of variability will relate to the main controlling parameters described in Section 2. Variation in biomass feedstock, even if nominally a single source, is likely to be one of the main causes of variability (Downie, 2009). The exact composition of a type of biomass will vary depending on many factors relating to when, where and how it was grown, for instance the weather, soil type and agricultural regime. Figures for carbon contents in nominally the same type of biomass may differ by as much as 10% relative (Gaur and Reed, 1995). The composition of a single supply of a particular biomass type should be more consistent but is not likely to be truly homogenous, except at small scale, unless special provisions for mixing and blending are made. Feedstock moisture content and particle size may vary within and between loads and affect process yields.

Temperature control is also likely to be an important cause of variability, particularly for slow pyrolysis. The lower heat fluxes and longer residence times of slow pyrolysis give scope for variation in heating rate and peak temperature. Yields from traditional charcoal kilns are known to be affected by weather conditions (Toole et al, 1961), due to the effect on temperature control and fuel-wood consumption. The BEST Energies slow pyrolysis demonstration plant is reported (Downie et al, 2007) to operate with a ±30°C temperature range under continuous steady-state conditions at 550°C and this is considered to be “a highly

controlled process" (Downie, 2009). Reference to the charts in Section 2 suggests this temperature range would lead to detectable variation in yield.

Fast pyrolysis, at least fluidised bed and similar systems, might be expected to have less variability due to the need for tight control of material and heat flows and the engineering design measures to achieve this. However, limited evidence suggests variability is no less for fast than for slow pyrolysis.

4.3 Evidence and Magnitude of Variability

Literature on pyrolysis reviewed for this study generally gives yield data as single values or as a range relating to different operating conditions. For single values, there is rarely any indication of whether this is an average of several experiments or one result. However, five reports were found where multiple yield data were given from the same, or very similar conditions and feedstocks.

These include two studies of traditional charcoal making, one involving masonry block kilns (Toole et al, 1961), one a simple oil-drum kiln (Okimori et al, 2003); these studies gave yields for charcoal only. Information on the Haloclean intermediate pyrolysis process (Hornung et al, 2006) gives yield data for char, liquid and gas for three runs at different temperatures, but within a range representing typical operational variation (375-400°C). Similarly, data for the Biotherm fast pyrolysis process (Dynamotive, 1999) gives yields for different temperatures (459-490°C) close to or within the stated design range (470-490°C). Data for the GRTI fast pyrolysis pilot plant (abandoned in 1989) also relate to a narrow range of typical operating temperatures (499-524°C) (Bridgwater and Peacocke, 2000). These data are summarised in Table 3 where an average, absolute range, and percent relative standard deviation (%RSD) is given for each set.

Table 3. Summary of Pyrolysis Yield Variability Data

		Data points	Char			Liquid			Gas		
			Ave. Yield	Range	%RSD	Ave. Yield	Range	%RSD	Ave. Yield	Range	%RSD
Process and Reference	**Feed**	#	% wt	% wt	%	% wt	% wt	%	% wt	% wt	%
Traditional charcoal making, block kilns, various feeds, (Toole et al, 1961)	Oak, maple, other hardwoods	16	28.2	9	8.7						
Traditional charcoal making, block kilns, single feeds, (Toole et al, 1961)	Seasoned maple (ave. 31% moisture)	6	29.5	5	5.8						
	Unseasoned maple (ave. 58% moisture)	5	26	3	4.2						
Traditiona charcoal making, drum kilns, (Okimori et al, 2003)	Acacia	3	25.4	2.6	4.6						
Intermediate pyrolysis, Haloclean process, rotary kiln with screw, (Hornung et al, 2006)	Wheat straw	3	36	5	5.4	38	7	7.5	26.1	10	16.1
Fast pyrolysis, Biotherm process, (Dynamotive, 1999)	Wood, undefined	4	21.3	9.5	16.3	64.4	20	12.3	13.9	15	42.8
Fast pyrolysis, GTRI process, entrained flow tube, (Bridgwater and Peacocke, 2000)	Wood, undefined	5	11.9	13.6	41.5	53.8	11.9	7.2	34.4	20.4	21.6
Fast pyrolysis, bench scale continuous fluidised bed, (Yanik et al, 2007)	Oreganum stalk		23		8	39		8			
	Corncob		23		7	41		2			
	Straw		20		2	35		4			

A further report (Yanik et al, 2007) stating a degree of variation of char and liquid yields for given conditions is also summarised in Table 3. This study used fast pyrolysis with a bench-scale continuous fluidised bed reactor at a fixed temperature (500°) and three different feeds. In Table 3 the stated variation is taken as standard deviation and converted to %RSD, however, this may be an over-estimate as it is not clear from the report if standard deviation or range is given.

This data appears insufficient to be statistically significant but may justify an opinion that variability in char yields from intermediate pyrolysis or charcoal making, and by implication slow pyrolysis, is of the order of 5%RSD. This would imply a likely variability of ±1.5% absolute in a typical slow pyrolysis char yield of 30%.

The data for liquid yields support a similar estimate of an order of 5%RSD variability, with the exception of data for the Biotherm process. However, if the data points from temperatures outside the Biotherm design range are excluded, the variability in the two remaining points is within this estimate. The gas yields appear to vary to a greater degree but the data is insufficient to generalise. Greater variability in gas yields could be rationalised as due to difficulties in measurement or collection of gas product but it may simply arise arithmetically through the usual calculation of gas yields from the mass balance; absolute errors or variability in liquid and char yields will add to give larger absolute error in gas yield.

Variability in char yield from the GTRI fast pyrolysis process looks to be greater than other processes, this may be related to the low char yield. It is not possible to conclude a clear difference in variability between fast and other pyrolysis processes from this data, although an impression of greater variability in fast processes may be given.

The views of industry experts on the causes and degree of variability in pyrolysis process yields were sought to substantiate the conclusions drawn. Adriana Downie of BEST Energies gave the following comments on sources of variability (Downie, 2009).

> "Yields change dramatically due to feedstock… the heat and mass transfer of the feedstock changes with composition and particle size distribution. These are the greatest factors that will determine the yield variability in any system… more often than not, the variables in the process outputs will come directly from the variability in the feedstocks."

The estimate of magnitude of char yield variability is given support by comments from Cordner Peacocke (2009):

> "When I've performed fast pyrolysis experiments on clean softwoods, I can usually get the char yields to be very consistent, within a few percent of the measured value."

Although this presents a view of consistency, it accepts a variability in line with the conclusion drawn above of an order of 5%RSD variability in product yields.

4.4 Sensitivity of Biochar System Benefits to Yield Variability

The significance of this estimated char yield variability has been examined using simple sensitivity analysis of four literature case studies, three focusing on carbon abatement outcomes, one considering financial viability of pyrolysis processes. In each case the calculations made in the study were repeated using char yields 5%(relative) lower and higher than used in the original report and sensitivity to the change was determined.

4.4.1 Case Study 1

A study by Okimori et al (2003) investigated potential carbon dioxide emission reductions through carbonisation of forestry wastes from acacia plantations in Indonesia. The wastes would be converted to charcoal in small, local facilities using drum, pipe or brick kilns with no capture of liquid or gas products for energy use. The char could be re-applied to soils in forest re-plantation or in agriculture leading to sequestration of carbon, although a market for charcoal for combustion was also recognised. A potential for sequestration of *ca.*48,500 t-C/yr was estimated from this activity given an annual plantation area harvested of 10,750 ha.

Applying the estimated relative variability in char yield of ±5% in this case study gave a directly proportional change of ±5% in the resulting benefit, implying a range of *ca.*46,000-51,000 t-C/yr potential carbon sequestration. This is displayed in Figure 5.

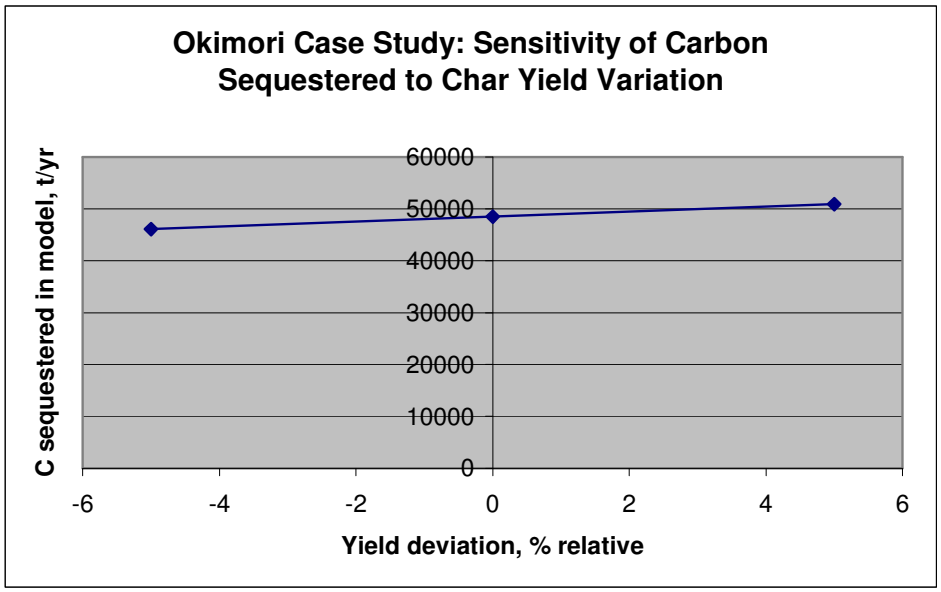


Figure 5. Okimori Case Study: Sensitivity of Carbon Sequestered to Char Yield Variation

4.4.2 Case Study 2

Ogawa et al. (2006) examined a number of cases for carbon sequestration through biomass carbonisation, two of which are considered here and in the following section. The first was based on acacia forestry in Indonesia, as above, but this time also combined with carbonisation of wastes from the associated pulp mill. The biochar produced would again be used for soil improvement in forestry and agriculture.

The total potential for carbon sequestration estimated in this case was 15,571 t-C/yr. Applying the ±5% char yield variability estimate to calculations in this study leads to a change of ±6% in benefit. The slightly exaggerated effect is due to an external fuel consumption allowed for in the calculation, assumed to be independent of char yield, and to the arithmetic effect of adding together the two halves of the case. The resulting range of benefit, 14,642-16,501 t-C/yr, is shown in Figure 6. This arises from a harvested forest area of 12,000 ha/yr, the lower benefit figure compared to the Okimori case described above is due to a lower assumed proportion of forest residues available for carbonisation.

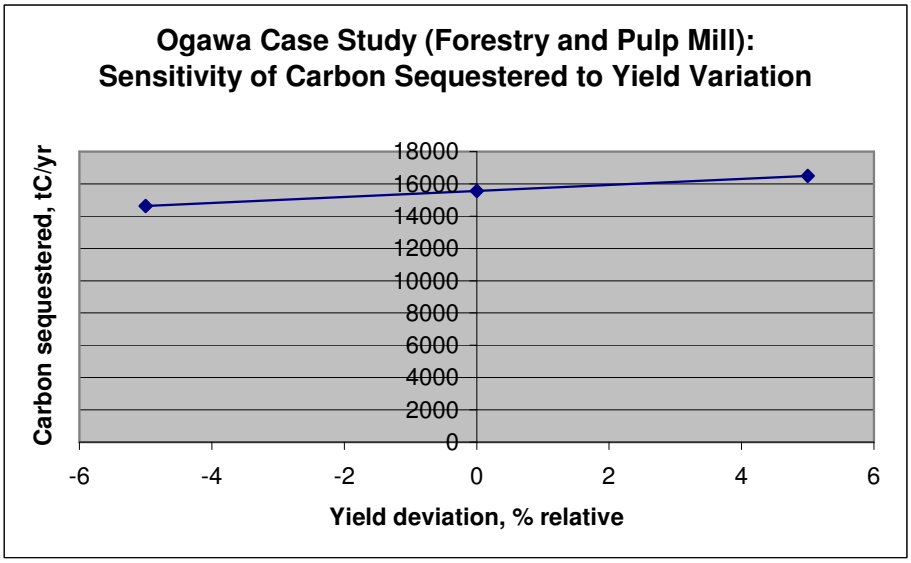


Figure 6. Ogawa Case Study (Forestry and Pulp Mill): Sensitivity of Carbon Sequestered to Char Yield Variation

4.4.3 Case Study 3

Another case studied by Ogawa et al (2006) involved mixing char produced from sawmill wastes with cattle manure to give a biochar compost used in agriculture in Japan on a small scale. This example combines benefits in waste disposal and carbon sequestration. Applying the same method as above gives a ±6% change in a projected benefit of 298 t-C/yr sequestered. The slightly exaggerated sensitivity compared to the ±5% yield variation is again due to a fuel use not proportional to char yield. The range of benefit, 280-316 t-C/yr, is shown in Figure 7.

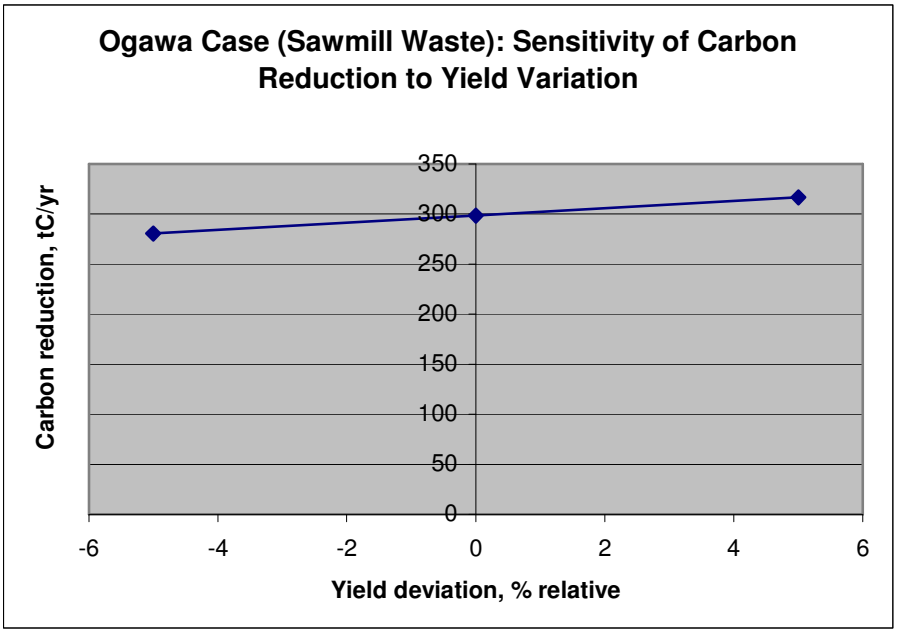


Figure 7. Ogawa Case Study (Sawmill Waste): Sensitivity of Carbon Sequestered to Char Yield Variation

4.4.4 Case Study 4

McCarl and co-authors (2009) present an economic analysis of the use of fast and slow pyrolysis for biochar production from maize stover (stalks and leaves) in the book *Biochar for Environmental Management* (Lehmann and Joseph, 2009). The analysis is based on data for the Biotherm fast pyrolysis process with estimates made to give corresponding information for an arbitrary slow pyrolysis process. The analysis assumes use of primary pyrolysis products as process energy source (all syngas and some char in the fast pyrolysis case) with all the liquid product converted to electricity. Excess char is available for soil amendment and is given a value in the analysis related to its greenhouse gas offset at contemporary prices. The use of about two thirds of the char product for process energy in the fast pyrolysis case, a feature of the Biotherm process (Dynamotive, 1999), leaves little available for greenhouse gas offset as soil amendment but maximises the liquid product availability for electrical generation.

The analysis considers capital and operating costs for the two processes balanced by revenue from electricity and biochar sales, and greenhouse gas offsets (McCarl et al, 2009). It predicts a negative net margin, or loss, in each case of –44.6 and –70.1 US$/t-feedstock for fast and slow pyrolysis respectively. Applying the estimated char yield variability of ±5% leads to only small changes in the estimated margins of ±0.8% for fast pyrolysis and ±1.2% for slow, as shown in Figure 8. The insensitivity of the net margin to biochar yield reflects the small proportion of the total represented by the biochar and greenhouse gas offset values compared to the value of electricity sales. The difference between fast and slow pyrolysis sensitivity is due to the greater availability of biochar product in the slow pyrolysis case.

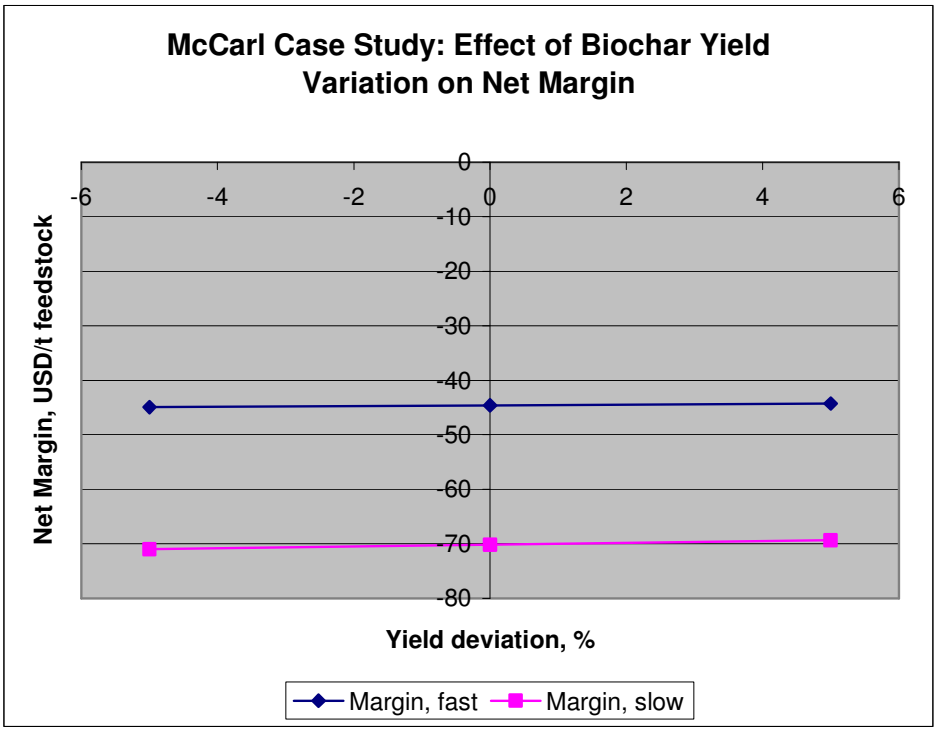


Figure 8. McCarl Case Study: Sensitivity of Financial Analysis to Char Yield Variation

4.5 Significance of Yield Variability

In any forecasting exercise, it is important to understand the accuracy that can be attached to a data set. The evidence for char yield variability in pyrolysis processes, while limited, suggests an order of ±5% RSD may be a reasonable estimate of variability. From the sensitivity analysis above it appears that variability in biochar system benefits may be exaggerated or

diminished compared to the variability in char yield depending on the way in which biochar contributes in the benefit calculation. In the examples given where the effect is exaggerated, this is due to a subtractive factor independent of char yield reducing the net benefit while the absolute change in benefit with yield variation remains the same; hence the relative change is exaggerated. It should be expected that such exaggeration would be more significant for cases where the benefits of biochar systems are more marginal

In each of the case studies presented, several assumptions have been made to arrive at the projections of biochar system benefits. The variation in benefits arising from char yield variability is generally no greater, and often smaller than the effect of other assumptions made, but it remains as an underlying, if low level, cause of uncertainty.

5 Modelling Pyrolysis Processes: A Comparison of Options

5.1 Introduction

It has been established above that biomass pyrolysis processes can be operated to deliver char, liquid and gas products across a wide range of product distributions depending on choice of feedstock, process type and operating conditions. At one end of the range slow pyrolysis of a high-lignin biomass at moderate temperature would give high yields of char with some liquid and gas. At the other end, fast pyrolysis of a high-cellulose biomass at a higher temperature would give mostly liquid product with some gas and a little char. The properties of the products will also change across the range. This raises the questions of where in the range is it best to operate and how best to use the pyrolysis products?

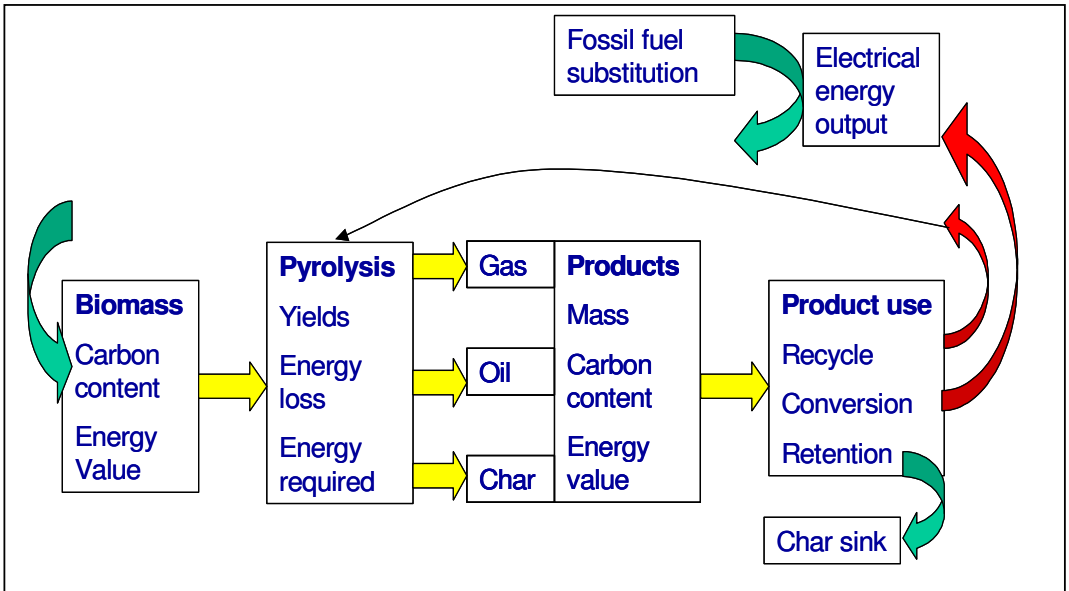
To answer these questions the criteria of what defines 'best' must first be decided. The increasing interest in biochar systems stems largely from the view that they may provide benefits across a number of areas. These include carbon sequestration from the atmosphere, improvement of soil fertility and productivity, avoidance of greenhouse gas emissions through fossil fuel substitution, or avoidance of emissions from waste disposal. The common theme is the climate change mitigation potential of biochar systems. In the present work this is taken as the overriding objective and so forms the main criteria of judgement for what is 'best'. However, it is important to recognise that other criteria have significant implications for the introduction and success of biochar systems, particularly financial criteria and the benefits for agriculture.

The second main objective of this project, covered in this section, is to understand how the range of pyrolysis process performance affects the benefits for climate change mitigation offered by biochar systems. The study focuses specifically on the effects of the pyrolysis process itself and the immediate downstream uses of the products. It is recognised that this is only part of a whole life-cycle assessment of the effects of biochar systems; the limitations of this simplification and some of the wider aspects are considered later in Section 5.8.

5.2 Methodology: Model Description

In Section 2.4 above a qualitative description was given of the carbon and energy flows associated with biomass pyrolysis and their effects on carbon dioxide in the atmosphere. The overall effect was described as the sum of two factors: the carbon dioxide emissions avoided through substitution of fossil fuels by use of pyrolysis products for energy; and the carbon stored in char through its equivalence to carbon dioxide removed from the atmosphere. A spreadsheet model has been constructed to calculate these two factors for different pyrolysis process examples and scenarios allowing comparison of their effects. Two main comparators are used: the net effect on carbon dioxide emissions and the electrical energy output available from the process.

The model is shown schematically in Figure 9. The figure highlights the main data requirements and the main carbon flows. The following sections describe the data required, some simplifying assumptions and the operation of the model in more detail.



Key:
Yellow arrows represent material and energy flow though the process.
Green arrows represent carbon dioxide assimilation, avoidance or sequestration.
Red arrows represent carbon dioxide emission.
Source: Author.

Figure 9. Schematic of Spreadsheet Model

5.2.1 Model Data Requirement

The model requires the following data to construct a complete balance for mass, carbon and energy and to derive the effects on atmospheric carbon dioxide.

- Carbon content (%C by weight) and energy value, taken as higher heating value (HHV), are needed for the material input and outputs of the process; that is, the biomass feedstock and the three product streams, char, liquid and gas.
- Process specific data are needed for the yields of each product stream (% weight on dry feed), the energy loss from the process, assumed to be heat loss (% feed energy content) and the energy requirement of the process (% feed energy content), that is the required inputs such as heat energy to achieve pyrolysis temperature or electrical power for drives.
- Conversion efficiencies (%) are required for each product stream being converted to electricity and for the biomass itself to provide a comparison with direct combustion.
- The carbon dioxide emission factor (CEF) is needed for a reference case for fossil fuel substitution, expressing the emission in carbon dioxide equivalents per unit of electricity generated in the reference case (kg-CO2e/kWh).
- An assumption is needed of waste heat availability from use of products for electrical generation (% energy input to conversion).

The actual case data used for modelling different processes and the issues of data availability are described in Section 5.3.

5.2.2 Simplifying Assumptions

The following simplifying assumptions are made for the model.

- All data relates to dry biomass feedstock. The step of drying the feedstock and its energy requirement are not modelled in detail, however, the model calculates the heat energy available as a check to confirm that there would be enough to dry the feed.
- It is assumed that heat released during electrical generation is re-used within the process for drying feedstock or other pre-heating duties; no external market for heat is assumed.
- The main energy requirement for pyrolysis is assumed to be supplied by recycle of a portion of one or more of the product streams; this is often the case in practice, particularly in scaled-up plant. Usually the gas stream is the first choice for recycle. Energy for initial start-up is not considered.

5.2.3 Operation of the Model

The operation and calculation method of the model are fairly simple and are described briefly here. An example print of a default model case is given in Appendix 3.

Data is manually entered in the 'Model Inputs' area for each case; carbon dioxide emission factors are entered in a separate area, as these are not usually changed between cases. Input data is transferred automatically to the calculation areas. Results are transferred out to the 'Model Outputs' area.

Based on the initial input data the model calculates balances for mass (from yields), energy (from yields and heating values) and carbon (from yields and carbon contents) summed over the three product streams. Given that in most cases modelled some of this data is estimated, it is usual that the energy and carbon are not balanced initially; if appropriate the estimates are adjusted to improve the balances to near 100%.

The model also calculates a 'process recycle' balance. This is initially zero and is brought up to 100% by adjusting the proportion of one or more of the product streams recycled to provide the process energy required. The remaining proportions of the products are available for conversion to electrical energy, or in the case of char, for carbon sequestration. However, an option is also provided in the model for char to be converted to electricity.

Once any data adjustments are complete and the model is balanced, the output data calculates automatically based on the following principles:

- The energy value of the portion of each product stream for conversion to electricity is adjusted by the conversion efficiency to give the electrical energy product.
- The carbon dioxide emissions resulting from use of each product stream, either through process recycle or electricity generation, are totalled.
- The above results are each summed across the three product streams to give totals for electrical energy product and carbon dioxide emissions arising from use of pyrolysis products.
- For the retained char available for carbon sequestration, the carbon dioxide equivalent is calculated from carbon content and the ratio of molecular/atomic weights.

- The total electrical energy product is used to calculate the avoided emissions due to fossil fuel substitution, by multiplying by the carbon dioxide emission factor; the model holds values for three reference cases.
- The net effect on carbon dioxide is calculated in two alternative ways:
    - 'Method 1' balances the carbon sink in the biomass used with the carbon emission from use of pyrolysis products adjusted by the avoided emission due to fossil fuel substitution (all expressed as carbon dioxide).
    - 'Method 2' considers the carbon retained in the char and the emission avoided due to fossil fuel substitution only (all expressed as carbon dioxide).
    - The methods converge when the carbon balance in the model is 100%. Only results from the more conventional Method 2 are used in the discussions following.
- A comparison calculation is made, following the same principles as above, for the alternative of using the same biomass feedstock directly for electrical energy generation by a combustion process.
- The heat available as a by-product of electricity generation is calculated from the energy value of each pyrolysis product stream used for generation and the heat conversion efficiency. The amount of water this heat would vaporise is calculated as a check on feedstock drying capability.

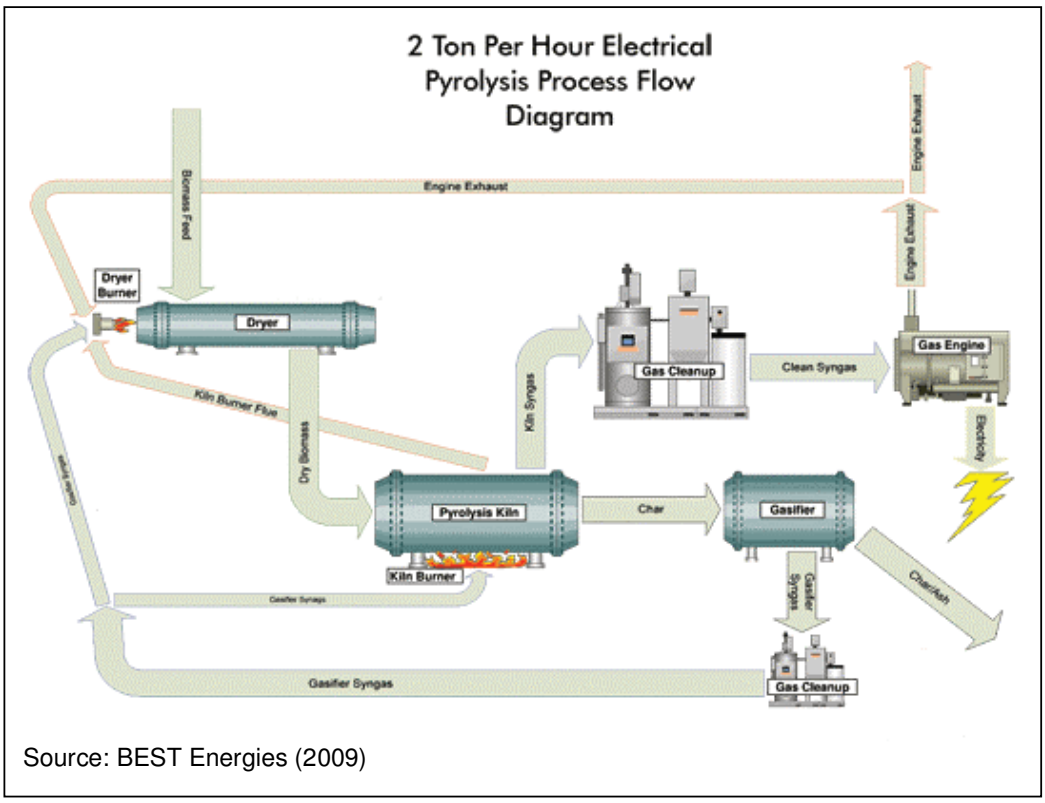
Finally, within the 'Model Outputs' area a number of ratios of primary results are calculated. In the output data, where not explicitly stated, all units are given per unit of dry feed with the default being per kilogram dry feed (kgdf).

5.3 Model Case Data

Review of the literature on pyrolysis described in Section 3 allowed the selection of a small number of cases for the modelling study. The selected cases cover slow, intermediate and fast pyrolysis processes being operated at pilot scale or larger, where reasonably adequate data, as required by the model, was published. In no case, however, was complete data found and missing values were estimated or drawn from other literature. The individual pyrolysis processes selected are described in the following sections. Data used for input to the model is collected for each case in Table 4. Comments on limitations of the data obtained follow in Section 5.3.5.

5.3.1 BEST Energies Pyrolysis Process

The BEST Energies process is one of the most well-known slow pyrolysis processes being promoted for biochar production, however, little technical data has been published on it. When contacted directly, Adriana Downie of BEST Energies, Australia, provided a reference with some data (Downie et al, 2007) and some useful comments (Downie, 2009). The process uses a continuously fed, agitated drum kiln with solids residence time believed to be around 30 minutes. It is operated at a higher temperature than normal for slow pyrolysis, typically 550°C. The process is also unusual in that no liquid product is isolated; the primary vapour product stream undergoes some form of treatment that is believed to convert the condensable vapours into further syngas. This results in a relatively high yield of syngas with a high heating value. An outline process flow diagram for a proposed commercial scale plant is given in Figure 10.



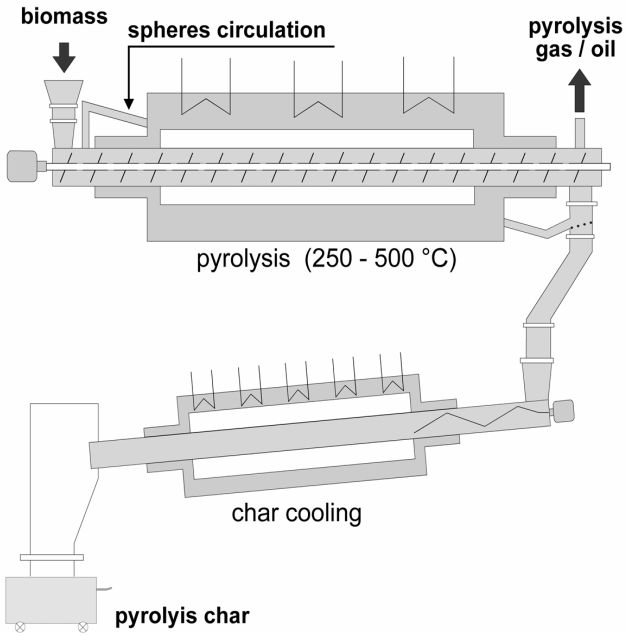
Source: BEST Energies (2009)

Figure 10. BEST Energies Slow Pyrolysis Plant: Outline Process Flow

Downstream of the pyrolysis kiln a gasifier may be used to convert char to further syngas, with the object of providing maximum gas yield for electricity generation. The data used in the model, given in Table 4, comes from pyrolysis of an undefined green-waste at 550°C, where the char was collected before gasification. It was obtained on a demonstration plant with 300kg/h dry feed capacity (Downie et al, 2007).

5.3.2 Haloclean Process

The Haloclean process is described as intermediate pyrolysis (Hornung et al, 2006). The technology was developed as a solution to treating plastic components in waste electrical and electronic equipment, but it appears to be finding a more promising application in the bio-energy area (Sea Marconi, 2009). It uses a rotary kiln with a rotating internal screw; metal spheres are used as an internal heat carrier. The solids residence times in the reactor are fairly short, 1-10 minutes. A pilot plant with feed rate of up to 100kg/h is established with plans for expansion to 500kg/h. A diagram of the pilot plant is shown in Figure 11.



Source: Hornung et al, 2006

Figure 11. Haloclean Pilot Plant Schematic

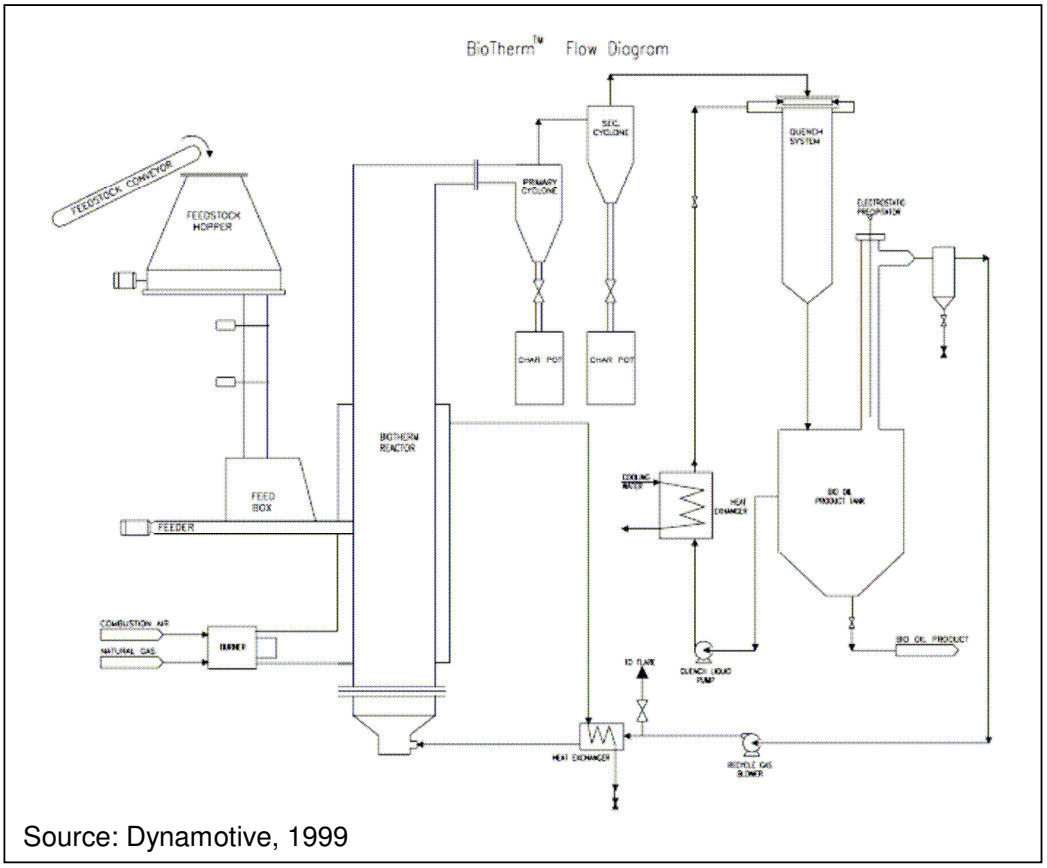
The data used in the model was, however, obtained on a bench-scale unit. The data refers to pyrolysis of finely ground wheat straw at 400°C and comes mostly from one key reference (Hornung et al, 2006) supported by other information supplied by Professor Andreas Hornung (2008) who has led the work developing the Haloclean process for biomass pyrolysis. Model input data used is given in Table 4.

5.3.3 Biotherm Fast Pyrolysis Process

The Biotherm process is one of the better-developed fast pyrolysis processes. A number of commercial plants are in operation for production of the liquid product, called bio-oil, at up to 200t/day feed capacity (Dynamotive, 2009). It has been developed through a partnership of Canadian companies: Dynamotive Energy Systems Corporation and Resource Transforms International Ltd. Again, limited technical data has been published on the process with most useful data coming from conference proceedings (Dynamotive, 1999; Radlein and Kingston, 2007).

The Biotherm system is a patented design (Piskorz et al, 1999) that uses a continuous deep fluidised bed reactor configuration. The claimed advantages are based on achievement of good quality bio-oil in high yield at relatively low temperatures, 450-500°C, and relatively long vapour residence times, 2-5s, compared to other fast pyrolysis systems. An outline process flow diagram is given in Figure 12.

The gas product stream is recycled for both fluidising gas and heat supply; however, additional energy input is needed also. In early designs this was supplied by natural gas but more recently through use of some char. The key reference (Dynamotive, 1999) is the only source found with concrete information on the process energy requirement and energy losses of pyrolysis processes. These are estimated to total 2.5MJ/kg feedstock or about 13% of the energy input in the feedstock, however, no information on the split between process requirement and loss is given. Full data used in the model is given in Table 4.



Source: Dynamotive, 1999

Figure 12. Biotherm Process Flow Diagram

5.3.4 McCarl Model Process

The economic analysis presented by McCarl et al (2009), previously discussed in terms of sensitivity to char yield variation, relates to fast pyrolysis based on the Biotherm process. The feedstock, maize stover, is different from the Biotherm case above and some of the data given differs significantly. This data is given in Table 4 and has been used in the model study to provide a comparison with the Biotherm case; it also allows a limited degree of benchmarking against the published outcomes of McCarl's analysis.

Table 4. Pyrolysis Process Model: Case Data

Model Inputs	Process	BEST	Haloclean	Biotherm	McCarl
Process Input					
Biomass type		Green waste	Wheat straw	Wood, undefined	Maize stover
Carbon content	%	45.6	43.2	50	46.5
Energy value	MJ/kg	17	15.9	19	18
Pyrolysis Process Data					
Mass Yield					
Gas	%	44.7	31.9	13	14.2
Liquid	%	15.3	34.6	72	70.9
Char	%	40	33.5	15	14.8
Energy loss	% input	6	0	3	17
Process energy	% input	10	10	10	9.70
Primary Process Output					
Gas					
Energy value	MJ/kg	13.1	11	11.5	3.9
Carbon content	%	37.37	30	36	32.45
Liquid					
Energy value	MJ/kg	0	12	17.9	17.9
Carbon content	%	0	30	46.5	46.5
Char					
Energy value	MJ/kg	25	24.7	27	11.4
Carbon content	%	72.3	70	78	60.29

KEY:
Data from key reference
Biomass data from Gaur & Reed (1995), other data calculated from key reference data
Estimate, or from balancing model, high uncertainty in some cases

Key Sources: BEST – Downie, et al, 2007; Haloclean – Hornung et al, 2008; Biotherm – Dynamotive, 1999; McCarl – McCarl et al, 2009.

5.3.5 Comments on Limitations of Model Study Data

The data in Table 4 have some clear limitations. No case has a complete set of data. This is somewhat surprising, but in each case there are commercial interests involved that may prevent full disclosure of technical information.

The feedstock data, where missing in the key references, have been estimated from Gaur and Reeds' *Atlas of Thermal Data* (1995) and checked where possible in an internet database (USDOE, 2009). An exception here is the energy value of the BEST process feed, an unspecified green-waste; the heating value has been estimated from the given carbon content by interpolation between other values in Table 4. Given the known variability in biomass

composition (see Section 4.2) these estimates will be a source of error in the model. A check on sensitivity to estimates of feed carbon content is described in Section 5.6.

For most model cases, the product yield data is given in the literature reference. An exception again is the BEST case where the gas yield is not given and no liquid is recovered. Analytical data for feed, char and gas (Downie et al, 2007) allow the gas yield to be estimated assuming all the carbon from the feed is partitioned between the gas and the char. The gas yield estimated (44.7%) implies there should be a liquid yield of 15.3%. This is rationalised for the model by assuming all the carbon and energy value of the primary liquid yield are transferred into the gas, resulting in the gas analysis given. The validity of this assumption is unclear; the argument may be circular, making this an area worth further investigation. The outcome of the BEST model case should be treated with caution.

No data on the energy loss or process energy requirement has been found for these cases other than the estimate mentioned above for the Biotherm process of a total of 13% of feed energy input (Dynamotive, 1999). An arbitrary split of this figure has been made allocating 10% to process energy and 3% to loss. The 10% process energy requirement has then been used as a default value in the other cases. Energy loss in the other cases is then derived by balancing energy across each model and will be subject to errors in other data, which are generally of better quality. No reliance should be placed on the loss figures but this has little effect on the main model outcomes.

Data for product energy values and carbon contents are also patchy. Missing data have been estimated as follows for each case.

Gas energy value in the Haloclean case is derived from charted data on ratio of gas to feed energy content (Hornung, 2008). The carbon contents of the three products have been estimated from an approximate relationship between energy and carbon content with adjustment to balance carbon over the model; different values of carbon content could also be chosen to balance. (The approximate ‘rule of thumb’ relationship scales heating value to elemental carbon content only, taking a value of 35MJ/kg for carbon, this gives a crude estimate generally underestimating heating value or overestimating carbon content.)

Gas analysis data for the BEST case (Downie et al, 2007) has been used to calculate gas energy value and carbon content using literature data for component gas heating values (Harrison, 1977). Energy value of the char has been estimated from the carbon content given.

Energy value of the gas from the Biotherm process has been estimated from data in the key reference (Dynamotive, 1999). The carbon contents of gas and char have been related to the energy contents and to balance across the model, the estimates appear somewhat high.

For the McCarl model case, the liquid values have been taken from the Biotherm literature (Dynamotive, 1999). The gas energy value and carbon content are calculated from the gas composition given in the key reference (McCarl et al, 2009; p346). The only gas components quoted are carbon dioxide, carbon monoxide and methane. Usually syngas contains hydrogen and C-2 gases also and the total heating value is highly sensitive to levels of these due to their high individual heating values. If contributions from these gases have been omitted in the gas composition given this might explain the unusually low value for gas energy calculated and would also affect the carbon content in the gas. The char has a low energy value quoted in the reference, this would indicate a low carbon content; the estimate made for the model is higher than indicated to balance carbon over the model. These possible under-estimates of energy values in the product streams also relate to the high figure for energy loss required to balance the model.

Although there are a number of uncertainties in the data, the model can still be used to compare broadly between process types and to indicate climate change mitigation effects. Some discussion of sensitivity to data inputs follows in Section 5.6.

5.4 Reference Case Data

The model calculates carbon dioxide emissions avoided when fossil fuel is substituted by use of a renewable, carbon neutral, energy source based on biomass for the generation of electricity. This requires a reference case for emissions from fossil fuel combustion. The model can hold and compare three reference cases. The case used as the main basis of discussion below relates to the average carbon dioxide equivalent emission from generation of UK grid electricity. Expression as carbon dioxide equivalent includes the contributions from methane and nitrous oxide emissions adjusted by their global warming potentials.

The carbon dioxide emission factor (CEF) varies over time with the mix of fuels used to provide UK grid electricity. It has decreased over recent decades with the trend away from coal toward gas use. Expressed as kilograms of carbon dioxide equivalent per kilowatt-hour of electricity (kg-CO_2e/kWhe) the CEF has fallen from 0.78 in 1990 to 0.55 in 2007 (DEFRA, 2009). Given this trend the UK government recommend using a CEF of 0.43 kg-CO_2e/kWhe for comparisons when considering renewable electricity (DEFRA, 2008) and this figure is used in the model as UK grid average reference case.

The other point of reference taken by the model is the alternative use of biomass feedstocks for direct generation of electricity, without pyrolysis. This is also a carbon neutral, renewable option that avoids greenhouse gas emissions by substituting fossil fuel combustion. To compare this option a figure for the conversion efficiency from biomass energy content to electrical output is needed. An arbitrary value of 33% conversion efficiency has been used in most model comparisons with the same figure used for pyrolysis product conversions. One exception is the liquid conversion efficiency in the McCarl case where a value of 36.9% was derived from the literature (McCarl et al, 2009). In reality the efficiency varies with the thermal-conversion and generating technology used and may range 25-30% for combustion or 20-40% for gasification (Thornley et al, 2009). Model sensitivity to different assumptions for conversion efficiency is discussed in Section 5.6.

5.5 Comparison Between Model Cases

To recap, the model described calculates the net effect on carbon dioxide emissions and the electrical energy output of biomass pyrolysis processes and compares this to alternative direct use by combustion of the biomass for electricity generation, both with reference to a projected UK grid average carbon dioxide emission factor. The model boundaries cover only the pyrolysis process and immediate use of products for electricity generation and it is limited by a lack of available data. Model outputs are all expressed relative to dry feed weight (kgdf).

Using the model case input data summarised in Table 4, with default values of 33% for electrical conversion efficiency and 40% for waste heat availability, the main model output data is given in Table 5.

Table 5. Pyrolysis Process Model: Output Summary

Model Outputs	Process	BEST	Haloclean	Biotherm	McCarl
Pyrolysis Product Conversion totals					
CO2 out	kg-CO2e/kgdf	0.61	0.73	1.44	1.61
Energy product	MJ/kgdf	1.37	2.00	4.25	4.68
Energy product	kWhe/kgdf	0.38	0.56	1.18	1.30
Char-C CO2e	kg-CO2e/kgdf	1.06	0.86	0.39	0.10
Energy / Char-C	kWhe/kg-C	1.32	2.37	11.22	48.59
Net CO2 benefit Substituting	kg-CO2e/kgdf				
Pyrolysis	UK Grid	-1.22	-1.10	-0.89	-0.66
Combustion	UK Grid	-0.67	-0.63	-0.75	-0.71
Relative CO2 Benefit Substituting	kg-CO2e/kWh				
Pyrolysis	UK Grid	-3.21	-1.98	-0.76	-0.51
Combustion	UK Grid	-0.43	-0.43	-0.43	-0.43
Available heat					
Heat product	MJ/kgdf	1.66	2.43	5.16	5.08
Heat product	kWht/kgdf	0.46	0.67	1.43	1.41
Overall efficiency					
Feed consumption	kgdf/kWhe	2.62	1.80	0.85	0.77
As electricity	%	8.07	12.60	22.38	26.02
As heat	%	9.78	15.27	27.13	28.20
Combined	%	17.85	27.87	49.52	54.22
Combusion Comparison					
Energy product	kWhe/kgdf	1.56	1.46	1.74	1.65

The key comparators calculated by the model, the electrical energy product and the net effect on carbon dioxide, are highlighted; they are plotted in Figure 13. The values differ between cases and are related (at least at a first approximation) to the different yields of pyrolysis products obtained by the processes. The electrical energy product is highest for the fast pyrolysis processes, where high liquid yields are obtained and used for power generation; it is lowest for the slow pyrolysis process where much of the energy value of the feedstock is locked in the char product. The net effect on carbon dioxide is negative for all processes showing there is a benefit to atmospheric carbon dioxide levels in each case arising from the combination of carbon sequestration in char and avoidance of emission from fossil fuel use. The magnitude of the benefit is greatest for slow pyrolysis, where most carbon is retained in the char, and least for the fast processes with low char yields, particularly for the McCarl model case, which consumes much of the char product for process energy. The differences across most of the data outputs can be linked back to the product yields in a similar way.

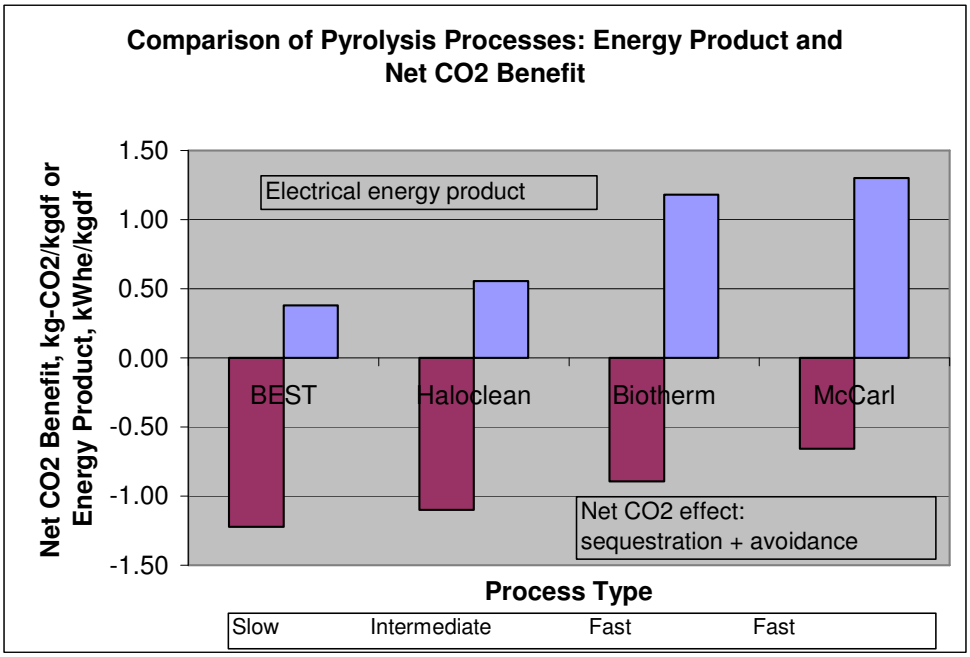


Figure 13. Comparison of Pyrolysis Processes: Energy Product and Net CO_2 Benefit

Display of the main comparators in Figure 13 shows a clear trade-off between net effect on carbon dioxide and electrical energy production. If the criterion for judgement of best use of a biomass feedstock is the effect on atmospheric carbon dioxide levels, then these results suggest that slow pyrolysis should be favoured over fast. This can be rationalised as the action of locking carbon into char having a greater effect than avoiding emissions from fossil fuel use. However, given the limited boundaries of the model this may be too simplistic a conclusion. Sensitivity to some of the main assumptions affects the conclusion and other criteria for judgement must be considered, these are discussed in later sections.

In all cases the direct combustion of biomass feedstock would give higher electrical output than use of pyrolysis. Outputs ranging 1.45 – 1.74 kWhe/kgdf are calculated for direct combustion from the heating values of the feedstocks (Table 5). In each case this is greater than the output from pyrolysis. Energy output from pyrolysis is reduced by the energy requirement of running the process, energy losses and the energy value of any char retained. The comparison in terms of net carbon dioxide effect, shown in Figure 14, suggests slow and intermediate pyrolysis gives greater benefit (a more negative effect) than combustion while

the differences for fast pyrolysis are marginal. This conclusion can be linked to the char yield and the carbon locked within it and is again subject to the limitations of the model.

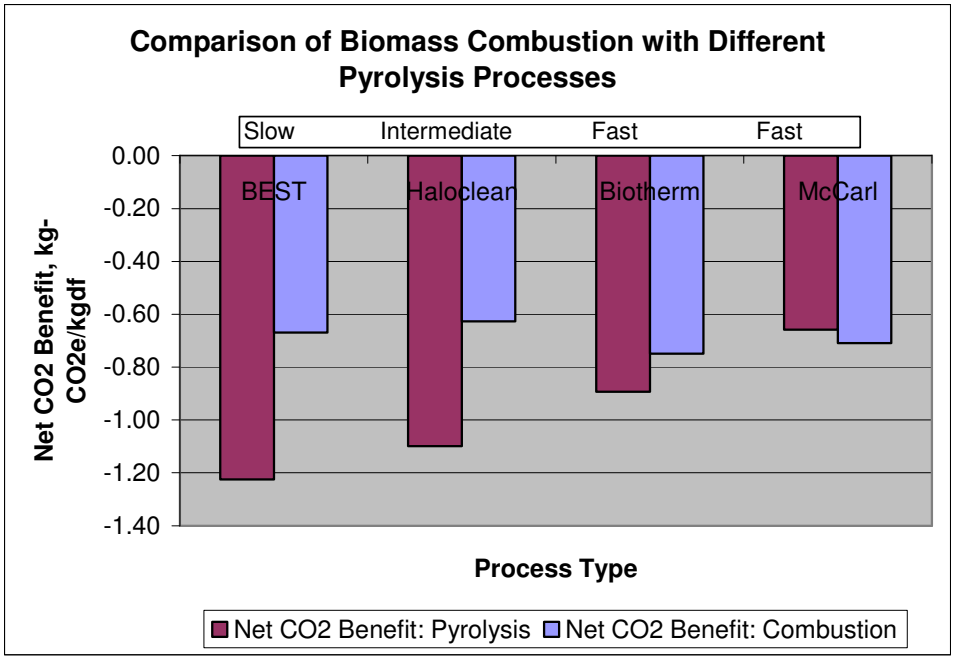


Figure 14. Net CO_2 Benefit of Biomass Combustion Compared with Pyrolysis Processes

In summary, the model comparisons suggest that slow and intermediate pyrolysis processes give greatest net benefit for atmospheric carbon dioxide, due to the carbon sequestered in char, but have low electrical output. Fast pyrolysis processes give greater electrical outputs than slow or intermediate pyrolysis but less than from direct combustion of biomass, they are little different from direct combustion in their net carbon dioxide effect when this is expressed relative to feed consumption. Relative to energy output, fast pyrolysis has greater (more negative) net carbon dioxide effect than direct combustion the margin depending on the quantity of char retained.

5.6 Benchmarking and Model Sensitivity

There are a few points where the model data outputs can be benchmarked against values reported in the literature.

Few previous estimates of the net carbon dioxide effect of pyrolysis biochar systems exist in the literature. Lehmann et al (2006) give figures for emission reductions of –1.8 to –2.4 kg-CO_2e/kg-feed-carbon for pyrolysis of wood waste with energy production and use of biochar in soils. Assuming 50% carbon content of the feed, these figures are equivalent to –0.9 to –1.2 kg-CO_2e/kgdf, close to the range of values estimated in this study. However, it is not clear what contribution to the carbon dioxide saving is from soil benefits in the literature figures.

In McCarl's analysis (2009) the net energy output of the fast pyrolysis process described is equivalent to 1.25 kWhe/kgdf; the model here gives 1.30 kWhe/kgdf. These values depend mostly on the liquid yield and energy content, their closeness implies little about the rest of the model; their difference is probably due to the estimate of energy content used in the model. McCarl et al (2009) also estimate greenhouse gas offsets for fast pyrolysis. Taking only the elements of their estimate that correspond to the current model would give a net effect as carbon dioxide equivalents of –0.85 kg-CO_2e/kg which is greater (more negative) than the figure returned by the model (-0.66) but close to that for the Biotherm fast pyrolysis process (-0.89), however, it is not clear what carbon dioxide emission factor has been used in their calculation.

The overall electrical efficiencies for the fast pyrolysis process in the model (22-26%) are in a similar range to those reported (20-30%) for ablative fast pyrolysis systems (Thornley et al, 2009; Meier et al, 2007). The combined heat and power efficiencies from the model (50-55%) are somewhat lower than reported (60-70%, e.g. Thornley et al, 2009) suggesting the estimate of percentage available heat energy used in the model is too low.

Sensitivity to a number of potential variables has been examined as follows.

Variation of ±5% in feedstock carbon content has been tested by adjusting the input value in the Haloclean case and determining the effect after re-balancing the model using estimates of product carbon content. This resulted in a change of <±3% in the output net carbon dioxide effect suggesting low sensitivity to inaccuracy in estimates of feedstock composition.

A set of model cases was run where the electrical conversion efficiencies were changed from the uniform 33% to test values of 45%, 37%, 33%, 25% respectively for gas, liquid, char and direct biomass conversion; these values chosen to represent more typical conversion

efficiencies for the materials. The main model outputs changed against the original values as shown in Figures 15 and 16. All pyrolysis cases become a little more carbon negative and have a higher energy product, combustion becomes less carbon negative, overall the change favours pyrolysis over combustion but the changes do not significantly affect any arguments.

A further set of model cases was run with the carbon dioxide emission factor (CEF) varying through 0.20, 0.43, 0.55 kg-CO_2e/kWhe. The low extreme represents a value for electricity generation by gas at high efficiency (IPCC, 2006); the high extreme is the value for UK grid average in 2007 (DEFRA, 2009). The results are shown in Figure 17.

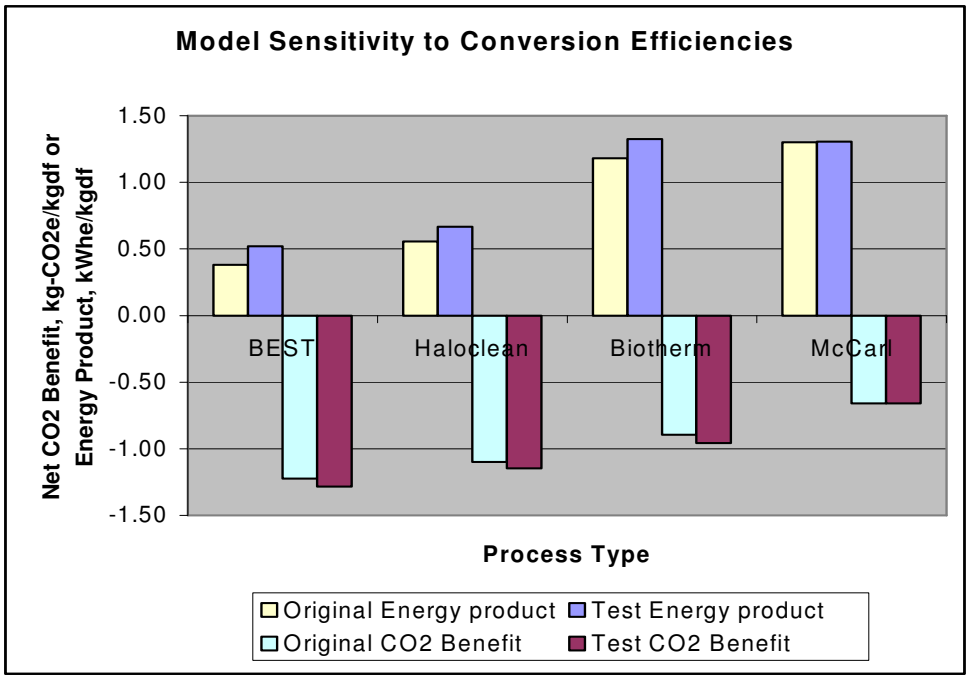


Figure 15. Model Sensitivity to Conversion Efficiencies: Energy Product and Net CO_2 Benefit

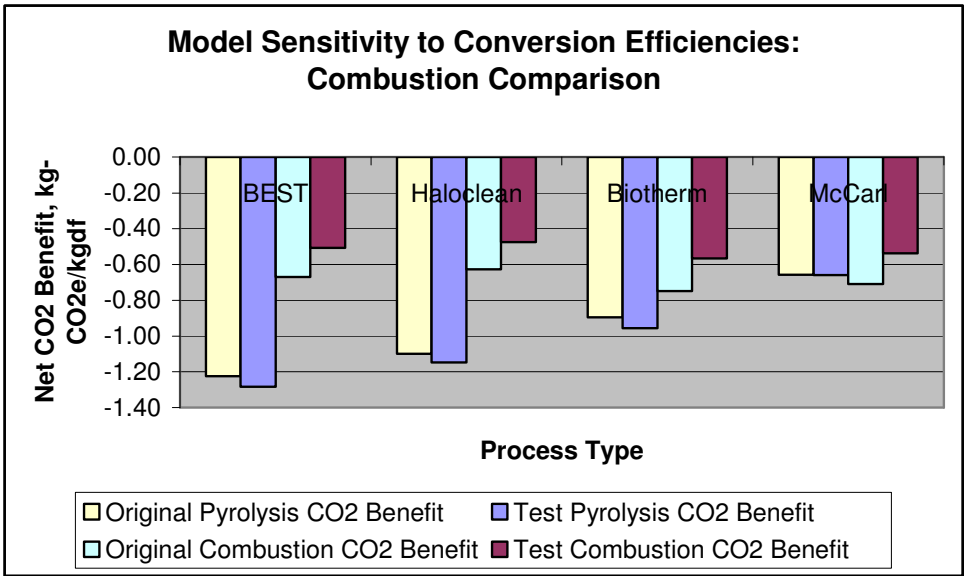


Figure 16. Model Sensitivity to Conversion Efficiencies, Combustion Comparison

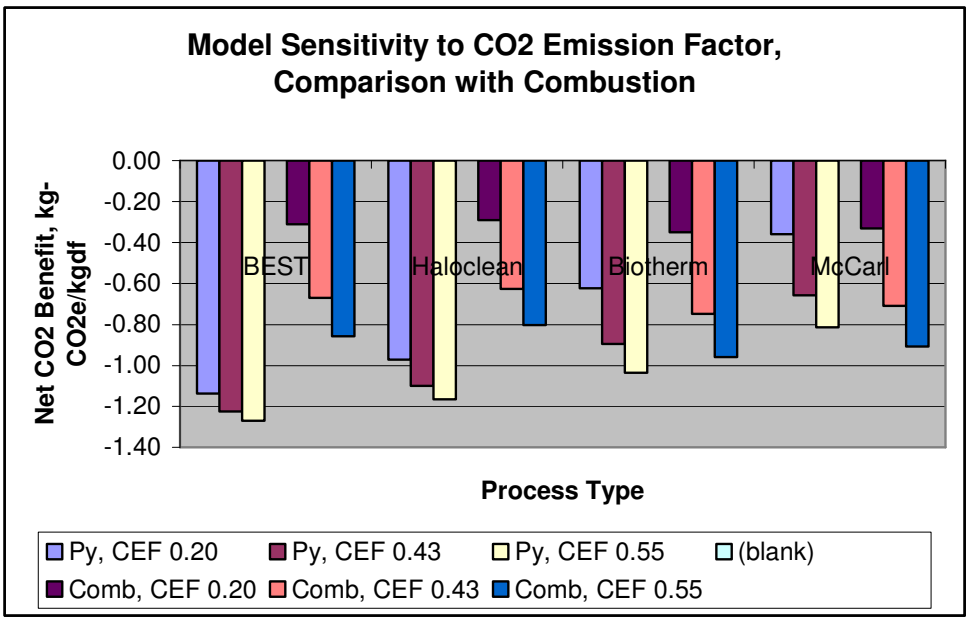


Figure 17. Model Sensitivity to Carbon Dioxide Emission Factor, Comparison with Combustion

This suggests that at high CEF values pyrolysis is less advantageous compared to combustion of biomass for electricity generation. For fast pyrolysis the advantage disappears. This can be rationalised as the effect of lower efficiency of pyrolysis being greater than the benefit of a small carbon sequestration as char. For slow pyrolysis there is still a benefit but the margin is reduced. At low CEF values, the relative advantage of pyrolysis due to carbon sequestration in char is increased over direct combustion and becomes more significant even for fast pyrolysis in the Biotherm case; the McCarl case has very little char so the difference remains marginal. Put another way, as the grid supply becomes less carbon intensive the benefit from replacing grid electricity by renewables diminishes, however, the benefit from sequestering carbon remains.

To summarise, within the limiting boundaries described earlier, the model appears to be fairly robust to some likely variables and some of the data assumptions made. Changes in model output are progressive and can be rationalised.

5.7 Scenario Modelling

Returning to the basic question addressed by the second main project objective, of where it is best to operate within the potential range for pyrolysis processes, an attempt has been made to use a series of artificial scenarios to probe where the optimum may lie.

A synthetic set of model data was constructed, based on a wood feedstock with process and product data related to slow or intermediate pyrolysis and default values of 10% each for energy loss and process energy requirement. With product yields initially set at 30%, 30% and 40% for gas, liquid and char respectively the output data was similar to the Haloclean model case for energy product (scenario 0.51, Haloclean 0.56 kWhe/kgdf). The net carbon dioxide benefit was somewhat higher (scenario -1.61, Haloclean –1.10 kg-CO_2e/kgdf), related to the higher char yield and a higher carbon content used to balance the model.

Scenarios forming a series with constant gas yield and varying liquid and char yields were each run through the model, balancing it using the char carbon and energy content at high char yields and the corresponding liquid values at high liquid yields. The yield variations are shown in Figure 18.

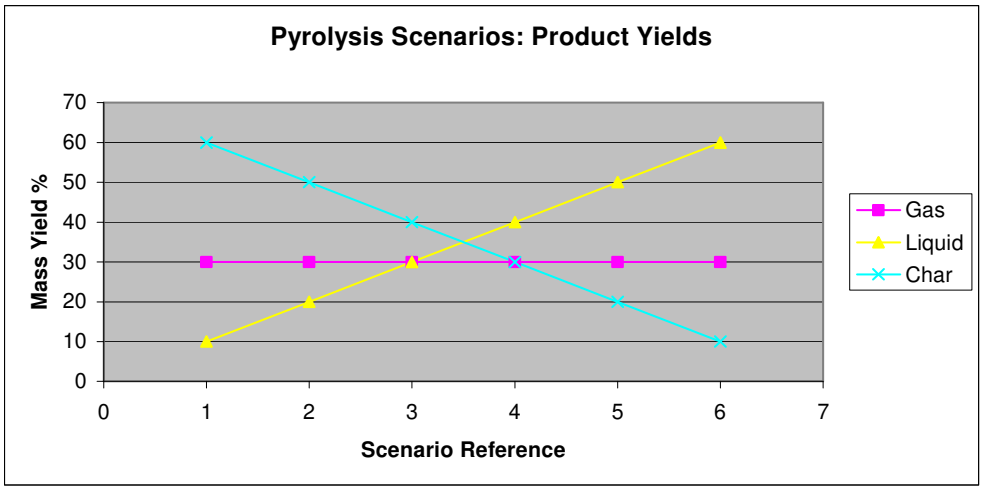


Figure 18. Pyrolysis Scenarios: Product Yields

For each scenario the standard model output data were recorded. Key data are displayed in Figures 19 and 20.

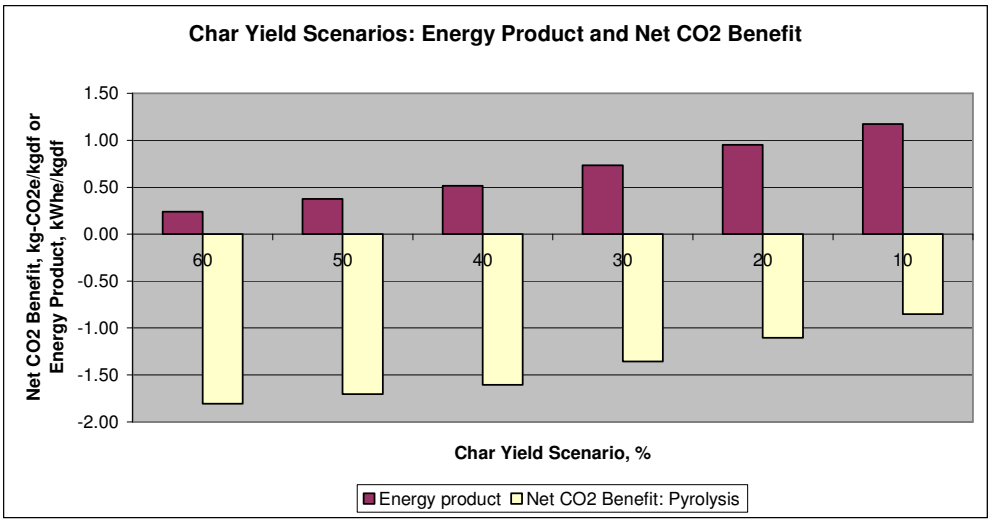


Figure 19. Char Yield Scenarios: Energy Product and Net CO_2 Benefit

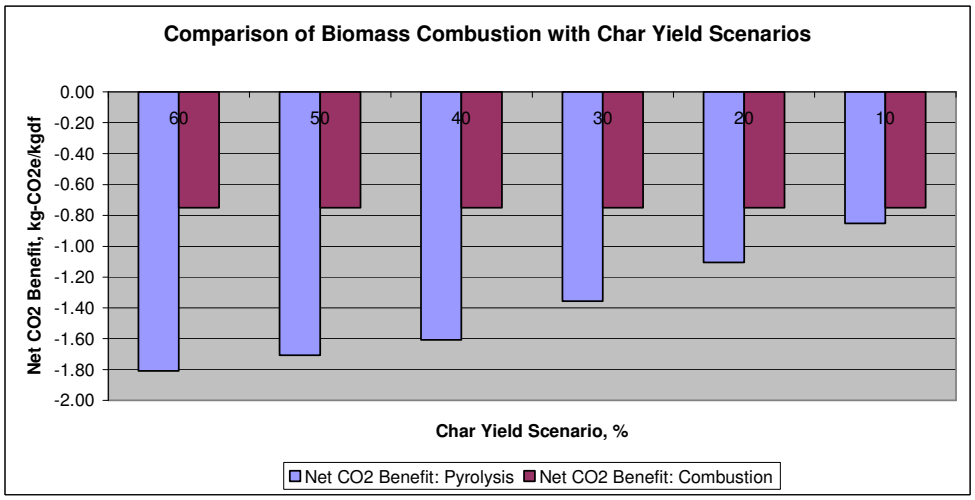


Figure 20. Char Yield Scenarios: Comparison with Combustion

These results show trends similar to the differences between slow, intermediate and fast pyrolysis. They emphasise the trade-off between running a process for benefit to atmospheric carbon dioxide and running it for electricity production. The trends are essentially linear and there is no optimum where both energy product and net carbon dioxide benefit are large (a slight change in slope between yield 30% and 40% results from the change in balancing method). Again the results also suggest that at high liquid, low char yields, such as achieved from fast pyrolysis, the advantage of pyrolysis over direct combustion of biomass for electricity generation is at best marginal for net carbon dioxide effect.

5.8 Relating Model to Reality

So far this discussion has been constrained by the limits of the model boundaries, that is, it has only considered the effects of pyrolysis processes themselves and the immediate downstream use of products for electricity generation. In this section the model is related to some important wider issues: financial aspects, the stability of biochar-carbon in soils and whole life-cycle analysis for biochar pyrolysis systems. These are treated briefly in the following sections.

5.8.1 Financial Aspects

The financial viability of pyrolysis systems will strongly affect their rate of establishment in current global society whatever their benefits in terms of climate change mitigation. The economic analysis of fast and slow pyrolysis by McCarl et al (2009) concludes that both would be loss-making with net margins of –45 and –70 US dollars per ton of feedstock respectively, on the basis of their assumptions. They consider three income streams, from electricity sales, greenhouse gas offset value from tradable carbon allowances and from biochar sales. The first two have recognised, if fluctuating, values; biochar value depends largely on agronomic benefits that are not fully demonstrated and so highly uncertain.

A simple financial analysis based on the outputs from the model described above has been carried out using recent UK values for industrial electricity (BIS, 2009) and EU Allowances for carbon dioxide (DECC, 2009); no value for biochar sales has been included. The model outputs from Table 5 for electrical energy product and net carbon dioxide benefit, for pyrolysis and combustion options, are multiplied by these values giving a total value for each case, results are shown in Table 6.

On this basis, the results suggest fast pyrolysis has around twice the income value of slow pyrolysis but that combustion of biomass for electricity generation has a greater value than all pyrolysis processes. The sensitivity of this outcome to values used has been tested and the general conclusions are robust. The price of electricity would have to fall by a factor of ten, to less than 1p/kWh, for the total values for fast and slow pyrolysis to become comparable with each other. Alternatively the value of the EU Allowance would have to rise by more than ten times, to over 130 £/t-CO_2e, for comparable values. Even greater changes in values of incomes would be needed for the pyrolysis and combustion cases to have similar outcome values

Table 6. Simple Financial Analysis

Price Factors			**Source**
Average UK industrial electricity price Q1 2009	p/kwh	8.4	BIS, 2009
Clearing price EU Allowance July 09	£/tCO2e	11.56	DECC, 2009
Clearing price EU Allowance July 09	p/kgCO2e	1.156	

		BEST	**Haloclean**	**Biotherm**	**McCarl**
Pyrolysis					
Energy value	p/kgdf	3.20	4.67	9.92	10.93
CO2 Value	p/kgdf	1.42	1.27	1.03	0.76
Total value pyrolysis	p/kgdf	4.62	5.95	10.96	11.69
Combustion					
Energy value	p/kgdf	13.09	12.24	14.63	13.86
CO2 Value	p/kgdf	0.77	0.72	0.87	0.82
Total value combustion	p/kgdf	13.86	12.97	15.50	14.68

However, there may be other ways of obtaining value from pyrolysis systems. Dynamotive Energy Systems, the operators of the Biotherm fast pyrolysis process have two commercial plants and aim to expand their operations further (Dynamotive, 2009). They aim to achieve higher added value by upgrading the initial bio-oil product into fuels suitable for transport use. The effect this will have on any greenhouse gas savings of the overall process is unclear, but it is likely to reduce the benefits.

In summary, these results suggest that financial considerations reinforce the trade-off between use of pyrolysis for climate change mitigation and for uses that are currently given a higher value by the economics of society, that is electricity generation or transport fuels.

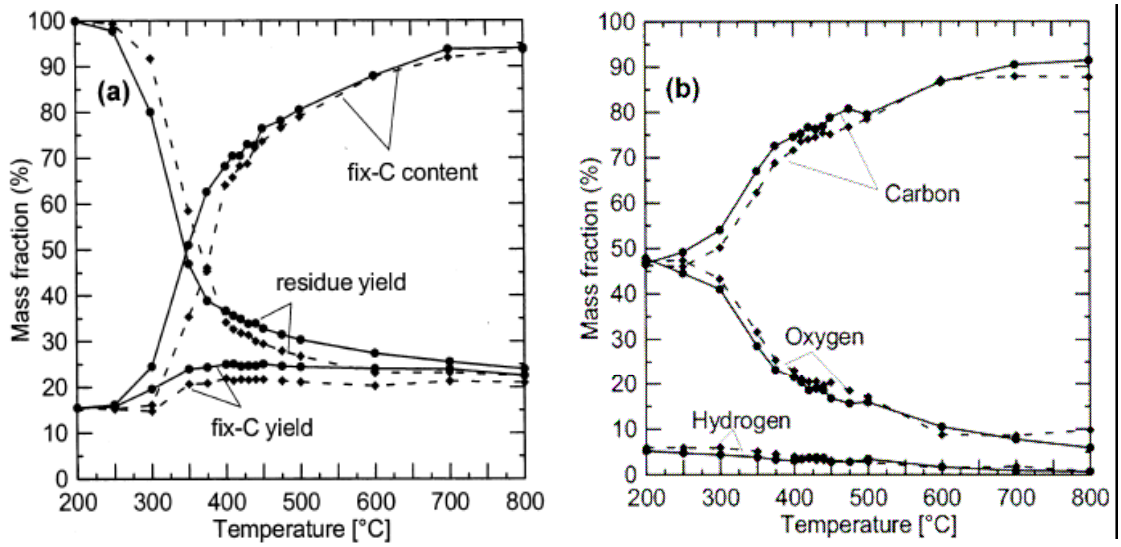
5.8.2 Stability of Biochar-carbon

Uncertainty over the stability of biochar when used as a soil amendment is one of the key areas of discussion and current biochar research. The subject is covered extensively in *Biochar for Environmental Management* (Lehmann and Joseph, 2009) and in other research literature.

There are indications that under some conditions biochar-carbon is stable for long periods, such as in Amazonian *terra preta* soils, but also that stability is specific to biochar properties and soil conditions and cannot be generalised (Lehmann et al, 2009). Typically, when biochar is mixed with soil, a portion of the carbon (the labile carbon) is lost in a fairly short time while the rate of loss of the remaining carbon is much longer. This more inert carbon may be related to so-called fixed-carbon but the relationship is not clear. Fixed-carbon is an analytical term for mass remaining in a char after adjusting for volatile material and ash, both determined by analytical pyrolysis (Antal and Grønli, 2003). Fixed-carbon will be less than total carbon by a margin depending on the temperature of pyrolysis; chars formed at lower temperatures will have more volatile carbon-containing material remaining than chars from high temperature pyrolysis. This suggests that high temperature chars, with higher fixed-carbon contents, may be more stable in soils than low temperature chars and there is some evidence to support this. Singh (unpublished data in Joseph et al, 2009) found that chars produced at 550°C in the BEST pyrolysis process had mean soil residence times an order of magnitude greater than chars produced from the same materials and process at 400°C.

Laboratory results showing the relationship between fixed-carbon content and temperature for a beech-wood char are shown in Figure 21 (Schenkel, 1999; reproduced in Antal and Grønli, 2003). Chart (a) shows lower char (residue) yields and higher fixed-carbon contents with higher pyrolysis temperatures as more volatiles are removed from the char at higher temperatures. The product of these values gives the fixed-carbon yield that plateaus, in this example, above about 350°C. Above this temperature chars will have successively higher fixed-carbon contents that may imply greater stability as biochar in soil. Also at higher temperatures a greater combined yield of volatile pyrolysis products (liquid and gas) may be expected. Conversion of these to electricity may be expected to improve the energy product of a slow pyrolysis process operated at higher temperatures. This is not shown in the model study above where the BEST Energies case has a pyrolysis temperature of 550°C; however, there are several uncertainties over the data used in this case. Unfortunately, fixed-carbon

contents of chars are rarely reported in the context of biochar so these suggestions are difficult to substantiate.



Source: Schenkel, 1999; in Antal and Grønli, 2003.

Figure 21. Laboratory Results: Relationship of Fixed-carbon to Pyrolysis Temperature

The loss of labile carbon from biochar in soils clearly reduces the carbon sequestration potential and needs to be considered in judging the benefits of pyrolysis systems. Estimates of the proportion of carbon lost, and in what period, vary (Lehmann et al, 2009) but a value of 25% loss in the first ten years has been used for assessing greenhouse gas effects (Gaunt and Cowie, 2009). The rate of loss beyond this is uncertain. A hypothetical model (Lehmann et al, 2009) suggests that if mean residence time for the so-called inert carbon is of the order of 1000 years, as expected by analogy with *terra preta* soils, the additional loss after 10 years is slow.

The effect of this carbon loss in the model cases discussed above has been demonstrated by adjusting the carbon dioxide equivalent retained in the char by a factor of 0.75. Selected key results from the modified model are shown in Table 7. Only the net carbon dioxide effect is changed by this modification. It leads to a smaller (less negative) net benefit in all pyrolysis cases, but with a greater proportionate effect for slow and intermediate pyrolysis due to their higher char yields. While these processes still have a higher net benefit than fast pyrolysis, the

difference is eroded significantly. The comparison against direct combustion also becomes less favourable for pyrolysis in all cases.

Table 7. Effect on Model of Reduced Biochar Stability

Model Outputs, Char Stability Factor 0.75	**Process**	**BEST**	**Haloclean**	**Biotherm**	**McCarl**
Pyrolysis Product Conversion totals					
Energy product	kWhe/kgdf	0.38	0.56	1.18	1.30
Net CO2 benefit	kg-CO2e/kgdf				
Substituting					
Pyrolysis	UK Grid	-0.96	-0.88	-0.80	-0.63
Combustion	UK Grid	-0.67	-0.63	-0.75	-0.71
Pyrolysis - Original model result	UK Grid	-1.22	-1.10	-0.89	-0.66

While these results do not change the general conclusions qualitatively – slow and intermediate pyrolysis still appear to provide greater net benefit for climate change mitigation than other options – the margin of benefit is significantly reduced when the effects of biochar-carbon stability in soils are included.

5.8.3 Whole Life-cycle Analysis

In terms of carbon accounting, or overall effect on carbon dioxide emissions, the model used above is limited to the boundary of the pyrolysis process and electrical generation. A whole-life-cycle approach would include contributions from effects upstream and downstream of these boundaries. Data has been provided for these contributions by Jim Hammond (2009, unpublished MSc dissertation) covering biomass production and transport operations, transport and spreading operations for biochar, and agronomic benefit from biochar in terms of effect on carbon dioxide emissions. The data is based on UK assumptions and covers two feedstocks, wheat straw and wood chips from UK forestry.

This data has been used together with outputs from the model described above to estimate the whole life-cycle effect on carbon dioxide emissions of the Haloclean and Biotherm processes, where pyrolysis data for these feedstocks is available. Model data assuming a char stability factor of 0.75 has been used and the effect of fossil fuel substitution has been separated out,

but remains included. The breakdown by life-cycle stage and the overall summation are shown in Table 8.

Table 8. Life-cycle CO_2 Effects: Haloclean and Biotherm Processes

Process	Haloclean	Biotherm
Feedstock	Straw	Wood
	kg-CO2e/kgdf	
Upstream		
Production	0.268	0.035
Transport	0.003	0.009
Sub-total	0.271	0.044
Pyrolysis and Conversion		
Biochar (at 0.75 stability)	-0.645	-0.290
Fossil fuels substitution	-0.239	-0.508
Sub-total	-0.884	-0.798
Downstream		
Transport and spreading	0.002	0.000
Agronomic benefit	-0.027	-0.016
Sub-total	-0.025	-0.015
Total Net CO_2 Effect	-0.638	-0.769

Source for upstream and downstream contributions:
Jim Hammond (2009, MSc dissertation)

These data, and comparison with figures in Table 7, suggest the upstream and downstream contributions for wood chips make only a small difference (<4%) to the outcome as total net effect on carbon dioxide emissions. For wheat straw the emissions from production modify the total net effect more significantly, reducing the benefit (less negative) by 28% from the model result. This reflects the intensive nature of wheat cultivation using fossil fuel based agrochemicals. Given the differences between the feedstocks it is not relevant to compare the two cases above as a way of comparing pyrolysis processes. Neither is it relevant to compare these outcomes with earlier figures for direct combustion, as these would also be modified by the upstream, if not the downstream, contributions.

In summary, the majority of the whole life-cycle effect on net carbon dioxide emissions offered by pyrolysis biochar systems can be related to carbon sequestered in char and

emissions avoided through fossil fuel substitution. Of the other life-cycle elements (with assumptions inherent in the supplied data) transport and farm operations have low significance; fossil fuel based agrochemical input to production is significant for some feedstocks. Agronomic benefit of biochar use has a small effect but is uncertain; the estimate given in the above figures is considered conservative (Hammond, 2009).

6 Conclusions

This study has focussed on the performance of biomass pyrolysis processes for use in biochar systems. The objectives have been to understand the range of control achieved by these processes and how this may affect the potential benefits offered by pyrolysis biochar systems. The benefits to climate change mitigation have been considered in particular for their importance to global environmental sustainability and as they form a common theme to the areas of benefit proposed for biochar systems.

There are several technologies capable of converting biomass to solid char products that may be suitable for use as biochar, often with liquid and gas co-products that can be used as fuels. Two main process types, slow and fast pyrolysis, plus the related intermediate pyrolysis have been reviewed to establish the scope of their operational control and variability. The main factors affecting yield distributions and properties of the products are the biomass feedstock itself (its composition and preparation) and the control of temperature and material flows during the pyrolysis process. Key factors are the peak reaction temperature and the gas environment affecting contact between primary solid and gas-phase products.

Product yield distributions from pyrolysis vary widely depending on feedstock, process type, reaction conditions and equipment used. These factors allow a degree of control over which main product, char, liquid or gas, is delivered through biomass pyrolysis. Typical mass yield ranges for slow pyrolysis are char 25-35%, liquid 20-50%, gas 20-50%; for intermediate pyrolysis, char 30-40%, liquid 35-45%, gas 20-30%; and for fast pyrolysis, char 10-25%, liquid 50-70%, gas 10-30%. In general slow and intermediate pyrolysis give higher char yields while fast pyrolysis gives higher liquid yields. Care should be taken when using such generalisations as there are important exceptions. For any comparison of biochar systems or their potential benefits to be meaningful the feedstock, pyrolysis process and outputs assumed should be clearly specified.

The variability associated with a particular yield figure for char from slow or intermediate pyrolysis has been estimated at ±5% (relative). Some support for this order of variability has been given by industry experts. The variability for liquid and gas yields or for yields from fast pyrolysis is less clear but may be of a similar order. Analysis of sensitivity to this char yield

variability has been carried out for some literature case studies of biochar systems. The effect is diminished or magnified depending on how char yield contributes to the calculation of system benefits. Char yield should be considered as an underlying source of variability in pyrolysis biochar systems although it is unlikely to be more significant than the effect of other uncertainties and assumptions.

The range of control of product distributions from biomass pyrolysis, through choice of feedstock, process and conditions, gives the potential to optimise the process to satisfy different objectives. Assuming a primary objective of maximising climate change mitigation, a model study has been used to compare three pyrolysis process types and direct combustion of biomass for their effect on greenhouse gas balance and their electricity generating capability. The effect on greenhouse gas balance, expressed as carbon dioxide equivalent, comes from two contributions, the sequestration of carbon in char and the avoidance of emissions when fossil fuels are substituted by renewable, biomass-based energy sources.

The model study suggests a clear trade-off exists for pyrolysis processes between benefit for carbon dioxide balance (net negative effect) and potential for electrical output. Processes that maximise char yield, slow and intermediate pyrolysis, give greatest net benefit for carbon dioxide balance due to the carbon sequestered in the char, but they have low electrical outputs. Fast pyrolysis, with higher combined liquid and gas yields, gives greater potential for electricity generation, although it is less than from direct combustion. Fast pyrolysis is similar in net carbon dioxide effect to direct combustion. Relative to energy output, fast pyrolysis has greater (more negative) net carbon dioxide effect than direct combustion the margin depending on the quantity of char retained. The comparisons can be summarised by the following trends:

Carbon dioxide benefit: Slow ≈ Intermediate > Fast ≈ Combustion
Electrical output: Slow < Intermediate < Fast < Combustion

The model sensitivity was examined and found generally robust. However, the reference case chosen for calculating avoided emissions when substituting fossil fuels is important. As the grid supply substituted becomes less carbon intensive the benefit from replacing grid electricity by renewables diminishes, however, the benefit from sequestering carbon in char

remains. This implies pyrolysis may become more favourable compared to direct combustion in future provided there is some retention of carbon in a stable form.

The initial model findings are self-consistent but are limited by the boundaries defined. The results were related to the important wider aspects of financial values, the effect of biochar stability in soil and the whole life-cycle for pyrolysis biochar systems.

Assuming current UK prices for carbon dioxide allowances and electricity a simple value analysis suggests that fast pyrolysis has around twice the income value of slow pyrolysis, but that combustion of biomass for electricity generation has a greater value than all pyrolysis processes. The trend can be summarised as follows:

Income value: Slow < Intermediate < Fast < Combustion

The stability of biochar-carbon in soils is one of the greatest uncertainties surrounding pyrolysis biochar systems and their potential benefits. Stability may be related to the fixed-carbon content of chars, which in turn is related to temperature of pyrolysis. This may give scope for improvement of biochar stability; however, the area is complex and dependent on many interrelated factors beyond the scope of this report. A simple modification to the model was made to show sensitivity to loss of 25% of biochar-carbon from soils over an initial period. This depresses the benefit to greenhouse gas balance arising from pyrolysis in proportion to char the yield. The trends summarised above remain but the margin of benefit is reduced for slow or intermediate pyrolysis and becomes negligible for fast pyrolysis compared with direct combustion. This is the most significant area of sensitivity examined for the model outcomes.

A simple whole life-cycle analysis based on the model has been carried out using figures supplied for upstream and downstream effects on greenhouse gas emissions. The cases examined were for intermediate pyrolysis of wheat straw and fast pyrolysis of wood chips; 25% loss of biochar-carbon from soils was assumed. Both cases are dominated by carbon-negative effects arising from carbon in char and fossil fuel substitution, that is, the effects covered by the original model. For wood chips other contributions are small, for wheat straw the emissions arising from intensive agriculture reduce the benefit (less negative) for greenhouse gas emissions.

A general summary of the conclusions of this study would be that the main benefits toward climate change mitigation offered by biomass pyrolysis processes come from the sequestration of carbon in char. If the objectives in using pyrolysis biochar systems are based on climate change mitigation then slow or intermediate pyrolysis with higher char yields should be preferred. The benefits from fossil fuel substitution are lesser and for fast pyrolysis the combined benefits may not be sufficiently different from direct combustion of biomass for electricity generation to justify use of pyrolysis.

This general conclusion is sensitive to the stability of carbon when present as biochar in soils. This is one of the major uncertainties of pyrolysis biochar systems and is an area of necessary and ongoing research. From the pyrolysis process point of view, research on how char properties affect stability would be beneficial, particularly to confirm the suggestion that higher pyrolysis temperatures may confer greater char stability through higher fixed-carbon contents. Other ways to maximise fixed-carbon yields might also be investigated, use of high pressure is one technique but alternatives suitable for simple pyrolysis equipment would be of interest. In any ongoing pyrolysis research and development, consistent quantification of carbon content and energy value of all process materials (feedstock and product streams) is recommended. This is essential to allow full analysis of the potential benefits for climate change mitigation or other effects of pyrolysis biochar systems.

References

Antal, M.J., Grønli, M. (2003) The art, science and technology of charcoal production. *Industrial and Engineering Chemistry Research.* **42**, (8), 1619-1640.

Antal, M.J., Mochidzuki, K., Paredes, L.S., (2003). Flash carbonisation of biomass. *Industrial and Engineering Chemistry Research.* **42**, 3690-3699.

BEST Energies Inc. (2009). BEST Energies web site BEST Energies Inc., Wisconsin, USA. http://www.bestenergies.com/companies/bestpyrolysis.html 12.08.09

BIS. (2009). *Energy Statistics: Prices.* Department for Business Innovation and Skills. London. http://www.berr.gov.uk/energy/statistics/source/prices/page47818.html 13.08.09

Blackwell, P., Riethmuller, G., Collins, M. (2009). Biochar application to soil. Chapter 12 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Bridgwater, A.V., Peacocke, G.V.C. (2000). Fast Pyrolysis Processes for Biomass. *Renewable and Sustainable Energy Reviews.* **4**, 1-73.

Bridgwater, A.V., Meier, D., Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry.* **30**, 1479-1493.

Brown, R. (2009). Biochar Production Technology. Chapter 8 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Canadell, J.G., Le Quere, C., Raupach, M.R., Field, C.B., Bruitenhuis, E.T., Ciais, P., Conway, T.J., Gillett, N.P., Houghton, R.A., Marland, G. (2007). Contributions to accelerating atmospheric CO2 growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proceedings of the National Academy of Sciences of the USA.* **104**, (47), 18866-18870.

Carbon Diversion Inc. (2009). Carbon Diversion Inc web site. Carbon Diversion Incorporated, Hawaii, USA. http://www.carbondiversion.com/Home 17.08.09

Day, D., Evans, R.J., Lee, J.W., Reicosky, D. (2005). Economical CO2, SOx, and NOx capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy.* **30**, 2558-2579.

DECC (2009). *Press Notice: Result of the Sale by Auction of 4.2 Million EU Allowances.* Department of Energy and Climate Change. London. http://www.dmo.gov.uk/documentview.aspx?docname=ETS/20090709auctionresult.pdf&page=ETS%20Auction 13.08.09

DEFRA. (2008). *Guidelines to Defra's Greenhouse Gas Conversion Factors for Company Reporting* DEFRA, London. http://www.defra.gov.uk/environment/business/reporting/pdf/ghg-cf-guidelines2008.pdf 13.08.09

DEFRA. (2009). *2009 Guidelines to Defra / DECC's GHG Conversion Factors for Company Reporting.* DEFRA, London. http://www.defra.gov.uk/environment/business/reporting/pdf/20090717-guidelines-ghg-conversion-factors.pdf 13.08.09

Demirbas, A., Arin, G. (2002). An Overview of Biomass Pyrolysis. *Energy Sources.* **24**, 471-482.

Demirbas, A. (2001). Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energy Conversion and Management.* **42**, 1229-1238.

Downie, A., Klatt, P., Munroe, P. (2007). Slow pyrolysis: Australian demonstration plant successful on multi-feedstocks. *Bioenergy 2007 Conference, Finland.*

Downie, A. (2009). Personal communication. 02.07.09

Dynamotive Energy Systems Corporation. (1999). BioTherm™ - a system for continuous quality, fast pyrolysis biooil. *Fourth Biomass Conference of the Americas.* http://www.biooil.ru/docs/1999OaklandBiomassPaper.pdf 15.08.09

Dynamotive Energy Systems Corporation. (2009). Dynamotive web site. *Corporate Presentation - Biomass into Synthetic Fuels.* Dynamotive Energy Systems, Richmond, BC, Canada. http://www.dynamotive.com/wp-content/themes/dynamotive/pdf/09.06.02-French-Delegation-Visit.pdf 14.08.09

Ensyn Corporation (2009). Ensyn Corporation web site. Ensyn Corporation, Wilmington, Delaware, USA. http://www.ensyn.com/tech.htm 17.08.09

Fowles, M. (2007). Black carbon sequestration as an alternative to bioenergy. *Biomass and Bioenergy.* **31**, 426-432.

Gaunt, J.L., Cowie, A. (2009). Chapter 18 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Gaunt, J.L., Lehmann, J. (2008). Energy balance and emissions associated with biochar sequestration and pyrolysis energy production. *Environmental Science and Technology.* **42**, (11), 4152-4158.

Gaur, S., Reed, T.B. (1995). *An Atlas of Thermal Data for Biomass and Other Fuels.* National Renewable Energy Laboratory, Golden, Colorado, USA.

Hammond, J.R. (2009). Unpublished MSc Dissertation. University of Edinburgh.

Harrison, R.D. ed. (1977). *Book of Data* Nuffield Foundation. Longman Group Ltd., London.

Henrich, E. (2007). The status of the FZK concept of biomass gasification. *The status of the FZK concept of biomass gasification.* Forschungszentrum Karlsruhe GmbH. Karlsruhe, Germany.

Hornung, A., Bockhorn, H., Appenzeller, K., Roggero, C.M., Tumiatti, V. (2004). *Plant for the thermal treatment of material and operation process thereof.* US Patent Application No.: 10/451018.

Hornung, A., Apfelbacher, W., Koch, W., Linek, A., Sagi, S., Schoner, J., Stohr, J., Seifert, H., Tumiatti, V., Lenzi, F. (2006). Thermo-chemical conversion of straw - Haloclean intermediate pyrolysis *17th International Symposium on Analytical and Applied Pyrolysis, 2006.*

Hornung, A. (2008). *Fast, intermediate or slow pyrolysis for fuels production, power generation from various biomasses or as pre-conditioning unit for gasifiers.* Presentation to Imperial College. Aston University. Birmingham, UK. http://www3.imperial.ac.uk/pls/portallive/docs/1/44315696.PDF 15.08.09

IPCC. (2006). *2006 IPCC Guidelines for National Greenhouse Gas Inventories.* Volume 2, Chapter 2. Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T., and Tanabe K. (eds). IGES, Japan. http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol2.html 18.08.09

Joseph, S., Munroe, P., van Zweiten, L., Cowie, A., Krull, E., Singh, Bp., Downie, A. (2009). *Biochar for Soil Fertility and Carbon Sequestration: a Review of Current Understanding.* Unpublished presentation. Australia and New Zealand Biochar Researchers Network.

Kammen, D.M., Lew, D.J. (2005). *Review of Technologies for the Production and Use of Charcoal.* National Renewable Energy Laboratory, Golden, Colorado, USA.

Kim, S.S., Agblevor, F.A., Lim, J. (2009). Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *Journal of Industrial and Engineering Chemistry.* **15**, 247-252.

Lehmann, J., Joseph, S. (2009). Chapter 1 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Lehmann, J., Gaunt, J., Rondon, M. (2006). Bio-char sequestration in terrestrial ecosystems - a review. *Mitigation and Adaptation Strategies for Global Change.* **11**, 403-427. http://www.cleanrg.com/Articles/Lehman(2006)%20-%20Bio-char%20Sequestration%20in%20Terrestrial%20Ecosyst.pdf 03.04.09

Lehmann, J., Czimczik, C., Laird, D., Sohi, S. (2009). Stability of Biochar in the Soil. Chapter 11 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Lenton, T.M., Vaughan, N.E., (2009). The radiative forcing potential of different climate geoengineering options. *Atmospheric Chemistry and Physics Discussions.* **9**, 2559-2608.

Lievens, C., Carleer, R., Cornelissen, T., Yperman, J. (2009). Fast pyrolysis of heavy metal contaminated willow: Influence of the plant part. *Fuel.* **88**, 1417-1425.

Lovelock, J. (2009). James Lovelock on Biochar: let the Earth remove CO_2 for us. *The Guardian.* 24th March 2009.

Mante, N.O.D. (2008). *Influence of Wood on the Pyrolysis of Poultry Litter.* Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA. http://scholar.lib.vt.edu/theses/available/etd-09082008-120932/unrestricted/Thesis-Pyrolysis.pdf 23.06.09.

McCarl, B.A., Peacocke, C., Chrisman, R., Kung, C-C., Sands, R.D. (2009). Economics of biochar production, utilization and greenhouse gas offsets. Chapter 19 in J. Lehmann and S. Joseph (eds) *Biochar for Environmental Management.* Earthscan, London.

Meier, D., Scholl, S., Klaubert, H., Markgraf, J. (2007). Practical results from PYTEC's biomass-to-oil (BTO) process with ablative pyrolyser and diesel CHP plant, in A.V. Bridgwater (ed.) S*uccess and visions for bioenergy.* CPL Scientific Publishing Service Ltd. http://www.pytecsite.de/pytec_eng/download.php?what=6 17.06.09

Michel, R., Mischler, N., Azambre, B., Finqueneisel, G., Machnikowski, J., Rutowski, P., Zimny, T., Weber, J.V. (2006). Miscanthus × Giganteus straw and pellets as sustainable fuels and raw material for activated carbon. *Environmental Chemistry Letters.* **4**, 185-189.

Mistry, P., Mouat, A., Campbell, K., Howes, P. (2008). *The Evaluation of Energy from Biowaste Arisings and Forest Residues in Scotland.* AEA Energy & Environment, report for SEPA, Glengarnock, UK http://www.sepa.org.uk/waste/waste_publications/idoc.ashx?docid=f27bd8f1-4789-4b6d-9be2-a88c9f552512&version=-1 17.08.09

Mohan, D., Pittman, C.U., Steele, P.H. (2006). Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy and Fuels.* **20**, (3), 848-889.

Monbiot, G. (2009). Woodchips with everything. It's the Atkins plan of the low-carbon world. *The Guardian.* 24th March 2009.

Ogawa, M., Okimori, Y., Takihashi, F. (2006). Carbon sequestration by carbonization of biomass and forestation: three case studies. *Mitigation and Adaptation Strategies for Global Change.* **11**, 429-444.

Okimori, Y., Ogawa, M., Takahashi, F. (2003). Potential of CO2 emission reductions by carbonizing biomass waste from industrial tree plantation in south Sumatra, Indonesia. *Mitigation and Adaptation Strategies for Global Change.* **8**, 261-280.

Peacocke, C. (2009). Personal communication. 07.07.09

Piskorz, J., Majerski, P., Radlein, D. (1999). *Energy Efficient Liquefaction of Biomaterials by Thermolysis.* US Patent No.: 5728271.

Pro-Natura. (2008). *Fighting climate change with green charcoal and increasing agricultural productivity.* Newsletter December 2008. Pro-Natura, Paris. http://www.pronatura.org/archives/200812_GreenCharcoal_en.pdf 15.08.09

Radlein, D., Kingston, A. (2007). The Potential role of Agrichar in the Commercialization of Dynamotive's Fast Pyrolysis Process. *International Agrichar Initiative Conference, 2007.* http://www.biochar-international.org/images/Agrichar_May2,_2007_Presentation-Radlein.pdf 15.08.09

Rocha, J.D., Olivares Gómez, E., Mesa Pérez, J.M., Cortez, L.A.B., Seye, O., Brossard González, L.E. (2002). The demonstration fast pyrolysis plant to biomass conversion in Brazil. *World Renewable Energy Congress VII.*

Schenkel, Y. (2009). *Modelisation des Flux Massiques et Energetiques dans la Carbonisation du Bois en Four Cornue.* PhD Dissertation, Universite des Sciences Agronomiques de Gembloux, Gembloux, Belgium.

Scott, D.S., Majerski, P., Piskorz, J., Radlein, D. (1999). A second look at fast pyrolysis of biomass - the RTI process. *Journal of Analytical and Applied Pyrolysis.* **51**, 23-37.

Sea Marconi. (2009). *Haloclean BioEnergy - Principles of Operation.* Sea Marconi web site. http://www.seamarconi.com/modules.php?name=News&file=article&sid=139 15.08.09

Sohi, S., Shackley, S., Masek, O., Thornley, P., Carter, S., Hammond, J.R., Brownsort, P.A., and others. (2009). Unpublished work. *Report for Defra Contract.* UK Biochar Research Centre, University of Edinburgh, Edinburgh.

Thornley, P., Upham, P., Huang, Y., Rezvani, S., Brammer, J., Rogers, J. (2009). Integrated assessment of bioelectricity technology options. *Energy Policy.* **37**, 890-903.

Titirici, M-M., Thomas, A., Antonietti, M. (2007). Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO2 problem? *New Journal of Chemistry.* **31**, 787-789.

Toole, A.W., Lane, P.H., Arbogast, C., Smith, W.R., Peter, R., Locke, E.G., Beglinger, E, Erickson, E.C.O. (1961). *Charcoal Production, Marketing and Use.* Forest Service, US Department of Agriculture. Report No.: 2213 http://www.fpl.fs.fed.us/documnts/fplr/fplr2213.pdf 15.08.09

US Department of Energy. (2009). Energy Efficiency and Renewable Energy, Biomass Program US Department of Energy. http://www1.eere.energy.gov/biomass/feedstock_databases.html 12.08.09

Yanik, J., Kornmayer, C., Saglam, M., Yuksel, M. (2007). Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. *Fuel Processing Technology.* **88**, 942-947.

Zanzi, R., Bai, X., Capdevila, P., Bjornbom, E. (2001). Pyrolysis of biomass in the presence of steam for preparation of activated carbon, liquid and gaseous products. *6th World Congress of Chemical Engineering, 2001.*

APPENDIX 1

Pyrolysis Process Literature Review

The following pages hold spreadsheet prints with information and summary data from the literature review of pyrolysis processes.

Copies of the spreadsheet may be available from the author or Dr Ondřej Masek, UKBRC, University of Edinburgh.

Process	Organisation	Source Ref	Pyrolysis Type	Process Temp, °C	Equipment Type	Status	Scale	Feed (data extracted)	Char Yield, %	Yield Basis	Oil Yield, %	Gas Yield, %	Comment
Lab-slow	CMK, Uni Hasselt, Belgium	Lievens et al, 2009	Slow	350	Static horrizontal tube	Lab	3g	Willow, leaves and branches, from contaminated land	54, 49.1	%w/w as fed (moist 12.3, 9.9%), including ash, 11.6, 3.4	33.9, 40.3, of which about 20 is water of reaction	<1	Low temp used to keep heavy metals in the char, but possibly not very charred at 350°C. High char yield includes ash, but if expressed on dry higher still - 61, 54.5% wt on dry
Lab-slow	RIT, Stockholm/ BAS, Sofia	Zanzi et al, 2001	Slow	550-750	Vertical tube of horrizontal rotating tube with sweep of inert, steam &/or co2	Lab	65g	Bagasse, miscanthus, olive waste, straw pellet, straw, salix, birch (Misc, Straw pel, salix)	24,25,12	%wt maf	66,63,39	10,12,49	Range of temps all high as trying to get activated carbon product. No energy values given. All done with activation gas sweep - steam in this paper. Other papers with inert gas Ar or N2, higher yields for char but little other data. Misc 30-45; straw 30-32.5%.
Lambiotte		Domac et al, 1985	Slow	Feed gas 900	Continuous vertical retort	Commercial	25000tpa Char	oak wood, <25% moisture and 10cm chunks	35	dry feed	some	?	Gas reused for process heat
Pyro-6F, Pyro-7 (Pro-Natura)	Pro-Natura	Pro-Natura, 2008 (Newsletter).	Slow	550	'Rotary Retort' (Horrizontal drum) - how driven?	Pilot, small 'commercial', few?	4-5 t char per day, (~500kg/h cont feed)	Mixed ag or for waste	30-45	on <15% moist feed (I.e. higher if expressed on dry)			Gas/vapours most consumed with excess of 120-150kW heat value for other uses. Need to search acedemia for more data.
Rectangular kilns		Rocha et al, 2002	Slow		Mechanical mat handling, vapour recovery	Trad	100t/month	wood	35-37	dry feed	small, 15-50 kg/month		Oil yield seems too low, Tonnes per month?
Reichert Retort	Aston, and Namibia Investment Centre	Domac et al, 1985; Honsbein, 2005	Slow	Feed gas 600-700	Semi/continuous vertical retort	Commercial	600 lt/40min	African woods	33-40	?	some	?	Gas reused, high-ish fixed-C implies a real high yield.
Research, slow py	Uni of Metz	Michel et al, 2006	Slow	400-600	Rotary kiln	Lab	10-30g bx	Miscanthus (M straw and pellets)	16-29	on dry	24-34	46-51	Gives variation for final temp (500,600), form (straw or pellet) heating rate (2.5-15 K/min). Oil yield includes water. No data on (non systematic) variability other than unexpected trend with particle size (larger->less char) which could be variability??
Rotary hearth		Domac et al, 1985	Slow	900-1000	Rotary hearth	Commercial	2-5000tpa char	fine wood or ag waste	25	dry feed	?	?	Gas and vapours burned for process heat or power
Rotary kilns	Terra Humana, Hungary	Someus, 1993 (US Patent)	Slow	up to 850	Rotary kiln	Commercial	100-250kg/h	any biomass, low grade coal					No yields given in patent or TH website. Link from //terrapreta.bioenergylists.org/company
Scientific Carbons	Scientific Carbons/Eprida /NREL	Yeboah et al, 2003	Slow	?	?	Based on Scientific Carbons Inc existing facility	Full scale ? 225kg/h of pyrolysis vapours, 50kg/h biomass pilot	Peanut shells	32	on dry feed (?)	31	5	Yields at pyrolysis output stage, plus water 32%. Output fed to reformer -> H2 57%, CO2 26%, CO 12%, CH4 5%.
Stennau	Uni of Tubingen	Bridgwater, Peacocke, 2000	Slow	'fairly low'	Rotary kiln	?	1t/d (41 kg/h)	MSW	56	daf???	30.9	71m3/t feed	solid yield seems high for true char yield on daf basis, maybe includes ash?
Tubingen	Uni of Tubingen	Bridgwater, Peacocke, 2000	Slow	300-350	Various: cone screw, rotary furnace, F-Bed, transport belt	commercialised	up to 400kg/h	sewage, msw, ag waste	50-60		18-27		Gives ele anal for char as 51% 'others' confirming high ash in this yield
VMR oven	eg Crarbo Group	Antal and Gronli, 2003	Slow		Twin cannisters	Established, eg Carbo Group	up to 11000tpa	various woods	30-32	?			Vapour/gas used for feed drying and process heat, Reumerman 2002 gives yield on dry of 41%.
Flash Carbonisation	Carbon Diversion Technologies	Antal et al, 2003	Pressure Slow	400-800	Pressurised reactor	Commercial	1t or 3.5t	any biomass	29.5-40	dry feed	*	*	Pressurised with an air input, ignition of biomass, but yield still approaching theoretical, off gas not flammable, ie the combustion is of gas/vapour, no oil recovered in Antal 2003 paper, but CDI show oil as a product. Yields from paper, CDI site quotes no yield.
ALTEN	Alten (KTI/ Italenergie)	Bridgwater, Peacocke, 2000	Intermediate	500	Fluidised/stirred bed	Pilot	500 kg/h	Wood/ ag waste	20.5	daf	20.5		But quotes 25% of each char and oil in text, gas yield 100/141 total mass input basis. P.11 of review
ALTEN	Uni of Thessaloniki / Italenegie	Zabaniotou and Karabelas, 1999	Intermediate	400	Fluidised bed	Pilot	9-1200kg/h dry feed	Forest res	15-20; 18	on dry feed			Plant uses air to fluidise and partial combustion for heat input. Oil and Gas yields not defined. Char separation poor and much ended up in the oil.
ALTEN		Zabaniotou and Karabelas, 1999	Intermediate						31.5	on dry feed	28.5	25	Zab quote of figures for Avezzano plant, 15% missing ?Water?

Process	Organisation	Source Ref	Pyrolysis Type	Process Temp, °C	Equipment Type	Status	Scale	Feed (data extracted)	Char Yield, %	Yield Basis	Oil Yield, %	Gas Yield, %	Comment
Haloclean	Aston, BioEnergy Research Group	Hornung, 2007and 2008 (unpublished presentations)	Intermediate	325-400	Tubular kiln, internal screw with steel balls		Pilots 50kg/h or 500kg/h ?	Detailed in pres	73-34	on dry feed (?)	18-42-35	9-32	Lowest temp may not be highly carbonised. Varies 48-34 over 350-400°C.Note probable typo giving 50% Char yield at 450° noted in other table (2005), corrected in 2008b.
Haloclean	Aston, BioEnergy Research Group	Hornung, 2008	Intermediate	450-550	Tubular kiln, internal screw with steel balls		Pilots 50kg/h or 500kg/h ?	Detailed in pres	15-41	on dry feed (?)	38-57	10-42	Pairs of results showing up to 18% variation in char yield for 50°C temp difference. Also gives charts with variation by feed form for straw - powder 38% pellets 45% at 375°C. Also pellets 45-35% for 375-400°C - so quite sensitive - useful data sets?
Haloclean	Sea Marconi, Italy	Sea Marconi, 2009	Intermediate	450-500	Tubular kiln, internal screw with steel balls	Commercialised, large scale for tyre also WEEE pyrolysis	2 tph biomass plant constructed (12000tpa)	Ag and For wastes	20-30	?	50-60	?	
Haloclean	FZK	Mai et al, 2008	Intermediate	450-500	Tubular kiln, internal screw with steel balls		Pilot 50kg/h	rape, rice, straw	20-40	on dry feed (?)	40-60	10-20	Possibly same work as Hornung reports. Yields from a chart - unclear. Quotes a 'water' yield which I think is really an aqueous organic fraction which is combustible in their engine.
Pyrovac	Pyrovac Inst. Inc.	Bridgwater, Peacocke, 2000	Fast-vacuum	450	Agitated tube, vac	commercialised	?	biomass, industrial and MS wastes (Fir/spruce bark, spruce wood)	34,24	dry feed	35,47	11,12	egs given for fir/spruce bark vs spruce wood. Integrated process burns char for elec and gas for process heat
ABRI/ROI	ABRI Inc and Renewable Oil International	Badger and Fransham, 2006	Fast?	?	Screw pyrolyser	Pilot and small commercial	50tpd (feed?)	wood, chicken manure	25	dry feed	60	15	Based on figures for wood in patent. Char from chicken manure 45% yield. ROI call process Fast Py. Patent saved not printed.
Ablative plate	Uni of Aston	Bridgwater, Peacocke, 2000	Fast	550-600	Hot plate, rotating blades	pilot	3kg/h	wood eg poplar	13.8-15.7	? Dry	74-80.8	6.2-10.4	Oil includes reaction water. Four runs given 550-602 °C - perhaps less variable?
Bioware	Uni of Campinas	Rocha et al, 2002	Fast	450-650	Fluidised bed	Large pilot	100kg/h	Various biomass	5-15	dry feed	70-75	15-20	
GTRI	GTRI	Bridgwater, Peacocke, 2000	Fast	500	entrained flow tube	Pilot dormant	~60kg/h	wood	7.6-21.2	daf	48.1-60.0	27.9-44.3	five runs quoted, reactor temps 499-524, showing variation, these were later runs once plant optimised, so indicative of variability
Lab-fast	Uni of Thessaloniki / CPRI	Ioannidou et al, 2009	Fast	360-730	Captive sample heated rapidly, no sweep gas?	Lab	0.3g	Corn cob and stalk	50-15	%wt as fed (?)	10-30	10-63	Neither of these set-ups seem very representative of large scale fast or slow processes
Lab-fast	Virginia Tech	Kim et al, 2009	Fast	450-550	Bubling FB	Bench scale	200g	Chicken and turkey litters, bedding material	22-44	%wt as fed (?)	15-29	32-61	
Lab-fast	Virginia Tech	Mante, 2008	Fast	450 (470)	Bubling FB	Bench scale	300g	Chicken litter, pine and oak shavings	43	%wt on dry	43	14	Pine:22,63,15. Same group as Kim 2007
Lab-fast	FZK	Yanik et al, 2007	Fast	500	Continuous FB	Bench scale	100g	Corncob, oregano stalk, straw	23,23,20	dry feed	39,41,35,	32,30,39	Plus 6% water in each case. Gives errors of +/- 1.9,1.4,0.4 on char yields. Residence times 1-2s.
Lurgi	FZK	Henrich, 2007	Fast	500	Twin screw pyrolyser	Large scale commercial for coal/shale /waste etc		straw, wood	20-30 straw, 15 20 wood	dry feed	50-60; 60-70		Aiming for oil for BTL process, although char included in the slurry for gasification. paper saved not printed
Rotating cone	BTG/ Uni of Twente	Bridgwater, Peacocke, 2000	Fast	600	Rotating cone	pilot	50-200kg/h	wood waste	15	?	60	25	BTG has/is scaling up
RTI Process/ BioTherm Process	Waterloo/RTI/ Dynamotive	Bridgwater, Peacocke, 2000	Fast										Not noted in detail as have other sources but does have some yield egs if needed
RTI Process/ BioTherm Process	Waterloo/RTI/ Dynamotive	Dynamotive, 1999; Radlein and Kingston, 2007	Fast	450-500	Continuous deep FB	Commercial	up to 200tpd	Wood; Bagasse	15;26	as fed (<10% moist)	72;62	13; 12	Gives good set of comparison and variance data. Char yield variability at design conditions ranges 4%, oil and gas ranges higher at low temps.
RTI Process/ BioTherm Process	Waterloo/RTI/ Dynamotive	Scott et al, 1999	Fast	475-525	Continuous deep FB	Commercial	up to 200tpd	Various biomass	12.5-30	dry feed	49-74	10-20	Gives data for hardwood sawdust, wheat straw, bagasse. Key to RTI process is discovery that longer vapour residence times don't adversely affect the oil yields in bubbling FBs.
RTP (Rapid Thermal Processing)	Ensyn	Bridgwater, Peacocke, 2000; Ensyn website	Fast	490	Transported bed updraft	Commercial	350t/d (14t/h)	eg woody	0		75 (Ensyn) up to 83		gas and char recycled for heat
Waterloo FPP	Union Fenosa, Sp	Bridgwater, Peacocke, 2000	Fast		Bubling FB	commercial	?2-4t/h	Eucalyptus, oak pine	15-20	dry feed	up to 70		gas recirculated
Waterloo/ Hamburg	BFH/IWC	Bridgwater, Peacocke, 2000	Fast	400-525 (475)	Continuous FB	Pilot	5kg/h	Contaminated wood	14.35	dry feed	72.4	13.25	
Wellman	Wellman Process Engineering	Bridgwater, Peacocke, 2000	Fast		Continuous bubbling FB	?Demonstration constructed 1999	250kg/h	Biomass	0		>70		Bridgwater consults for them?? Not sure of status. Char and ?gas consumed.
WFPP		Piskorz et al, 1996 (RTI Patent)	Fast	425	Continuous shallow FB			Hardwood sawdust	30.5	?	59.6	5.9	RTI Patent gives 'poorer looking' data from WFPP for comparison.
WFPP	Uni of Waterloo	Scott et al, 1985	Fast	450-650	Continuous shallow FB		Bench	Wood, ag and for wastes. Data for corn stover	45.7-19	as fed (9%moist, 11% ash)	21-32	11-14	Gives various other yield data in charts for other feeds. Char yields 25 35 at 400-450°C, but oil optimum temp 500-550. Might be worth getting the Canadian patent for WFPP

APPENDIX 2

Pyrolysis Process Information: Data Extracted for Selected Feeds

The following pages hold spreadsheet prints with data extracted from literature for the selected feedstocks: chicken litter, corn cob, corn stalk, miscanthus, pine, spruce, wheat straw, and willow. Data for the BEST Energies process using an undefined green-waste is also included.

Copies of the spreadsheet may be available from the author or Dr Ondřej Masek, UKBRC, University of Edinburgh.

Pyrolysis Process Information: Data Extracted for Selected Feeds							Update:	24.06.09	(references later)						
Reference									**Feedstock**						
Process	**Source Ref**	**Organisation**	**Country**	Type	Source	Moisture	Volatiles	Fixed-C	C	H	N	O	Other info	Particle size	Energy
						wt% wet	wt% wet	wt% wet	wt% on dry	wt% on dry	wt% on dry	wt% on dry		mm	MJ/kg
Lab-fast	Kim et al, 2009	Virginia Tech	USA	Chicken litter	Shenendoah valley, Virginia	22.81			37.15	5.3	3.13	34.67	Ash 22.8%	#20 mesh	15.14
Lab-fast	Mante, 2008	Virginia Tech	USA	Chicken litter	Shenendoah valley, Virginia	8-10			29.15	4.1	6.42	36.56	Ash 23.53%wtmf; S 0.36; Cl 0.62	1	14.79
Lab-fast	Ioannidou et al, 2009	Uni of Thessaloniki / CPRI	Greece	Corn cob	Orestiada, Greece	7.57	84.37		43.77	6.2		50	Ash 8.06%wt	<1	18.25
Lab-slow	Ioannidou et al, 2009	Uni of Thessaloniki / CPRI	Greece	Corn cob	Orestiada, Greece	7.57	84.37		43.77	6.2		50	Ash 8.06%wt	<1	18.25
Lab-fast	Ioannidou et al, 2009	Uni of Thessaloniki / CPRI	Greece	Corn stalk	Orestiada, Greece	6.44	91.26		43.8	6.4		49.78	Ash 2.3%wt	<1	18.17
Lab-slow	Ioannidou et al, 2009	Uni of Thessaloniki / CPRI	Greece	Corn stalk	Orestiada, Greece	6.44	91.26		43.8	6.4		49.78	Ash 2.3%wt	<1	18.17
Bio-Alternative	Birdgwater, Peacocke, 2000	Bio-Alternative	Switzerland, Spain	Fir wood (and others)		10-15							Dried and comminuted		
Pyrovac	Birdgwater, Peacocke, 2000	Pyrovac Inst. Inc.	Canada	Fir/Spruce bark		15							Dried and shredded		
Lab-slow	Zanzi et al, 2001	RIT, Stockholm/ BAS, Sofia	Sweeden/ Bulgaria	Miscanthus		6.6			48.9	4.6	0.4	46.7	Ash 2.69 %wtmf	1-3.2	
Bioware	Rocha et al, 2002	Uni of Campinas	Brazil	Miscanthus or other Elephant grass - not specified		10-12							Ash 11%wt on dry	2-4	
Bioware	Rocha et al, 2002	Uni of Campinas	Brazil	Miscanthus or other Elephant grass - not specified		10-12							Ash 11%wt on dry	2-4	
Research, slow py	Michel et al, 2006	Uni of Metz	France	Miscanthus pellets	Germany 2005	9.6	80		47.1	5.4	0.44	44.6	Ash 2.3; S 0.06; Cl 0.074. Cell 45; hemicell 30; lignin 21.	dia 6; length 10-30	17.744
Research, slow py	Michel et al, 2006	Uni of Metz	France	Miscanthus straw	Germany 2005	9.6	80		47.1	5.4	0.44	44.6	Ash 2.3; S 0.06; Cl 0.074. Cell 45; hemicell 30; lignin 21.		17.744
RTI Process/ BioTherm Process	Dynamotive, 1999	Waterloo/RTI/ Dynamotive	Canada	Pine 85%, spruce 15% mix	Local (Vancouver)	5							Ash 0.25%wt	<1.2	
Fixed bed	Ryu et al, 2007	Uni of Sheffield	UK	Pinewood		8.9	78.8	12.1	52	7		41		cube 20	17.8
Lab-fast	Mante, 2008	Virginia Tech	USA	Pinewood shavings	Shenendoah valley, Virginia	8-10			46.53	5.9	<0.5	42.31	Ash 1.95%wtmf; S <0.05; Cl 180ppm	1	18.02
WFPP	Scott et al, 1999	Uni of Waterloo	Canada	Spruce sawdust		7							Ash 0.46 (%wtmf)	1	
Lurgi	Henrich, 2007	FZK	Germany	Spruce wood		8.9							Ash 1%		16.2
Haloclean	Hornung, 2008	Aston, BioEnergy Research Group/FZK	Germany/UK	Wheat straw pellets											
Lab-slow	Zanzi et al, 2003	RIT, Stockholm/ BAS, Sofia	Sweeden/ Bulgaria	Wheat straw pellets		6.9			47	6.1	0.5	46.4	Ash 6.34 %wtmf	1-3.4	
Haloclean	Hornung et al, 2006	Aston, BioEnergy Research Group/FZK	Germany/UK	Wheat straw powdered											
Lab-slow	Lievens et al, 2009	CMK, Uni Hasselt, Belgium	Belgium	Willow (branches)	Limberg, contaminated land	10			45.5	6.1	0.7	44	Ash 3.4% wt on dry, CL-150ppm	<2	16
Lab-slow	Lievens et al, 2009	CMK, Uni Hasselt, Belgium	Belgium	Willow (leaves)	Limberg, contaminated land	12			41.9	5.7	2.1	37.8	Ash 12% wt on dry, S 0.9; Cl- 4650 ppm	<2	14
Lab-slow	Zanzi et al, 2002	RIT, Stockholm/ BAS, Sofia	Sweeden/ Bulgaria	Willow (salix)		7.3			48.8	6.2	1	43.4	Ash 0.75 %wtmf	1-3.3	
BEST Energies	Downie et al, 2007	BEST Pyrolysis Inc	Australia	'Greenwaste'		38			45.6	5.3	0.15	38.4	Ash 3.5% on dry; S 0.06%.		

Pyrolysis Process Information: Data Extracted for Selected Feeds								
Reference		**Process**			**Conditions**			
Process	**Source Ref**	Type	Equipment	Scale	Temperature	Pressure	Heating rate	Residence time
					℃	Mpa	℃/min	?
Lab-fast	Kim et al, 2009	Fast	Bubling FB	Bench - 200g/h here	450		fast	0.5-5
Lab-fast	Mante, 2008	Fast	Bubling FB	Bench - 300-350g/h here	469		fast	
Lab-fast	Ioannidou et al, 2009	Lab fast	Captive sample heated rapidly, low He sweep gas rate	0.3g	520	0.1	52℃/sec	?
Lab-slow	Ioannidou et al, 2009	Lab slow	Fixed bed, sample blown onto preheated beads, higher N2 sweep gas.	1.5g	500	0.1	Contact with preheated beads	>15min
Lab-fast	Ioannidou et al, 2009	Lab fast	Captive sample heated rapidly, low He sweep gas rate	0.3g	520	0.1	45℃/sec	?
Lab-slow	Ioannidou et al, 2009	Lab slow	Fixed bed, sample blown onto preheated beads, higher N2 sweep gas.	1.5g	500	0.1	Contact with preheated beads	>15min
Bio-Alternative	Birdgwater, Peacocke, 2000	Conventional carbonisation	Counter current updraft gasifier	50-2000kg/h	?	0.1		
Pyrovac	Birdgwater, Peacocke, 2000	Fast-vacuum	Agitated tube, vac	2880 kg/h dried (15%) biomass	450	0.015		
Lab-slow	Zanzi et al, 2001	Lab slow pyrolysis with carbon activation by steam	Vertical tube in furnace - packed bed?	65g	550		25	60min
Bioware	Rocha et al, 2002	Fast with partial combustion	Fluidised bed	Large pilot 100kg/h	450-500			
Bioware	Rocha et al, 2002	Fast with partial combustion	Fluidised bed	Large pilot 100kg/h	550-650			
Research, slow py	Michel et al, 2006	Lab slow pyrolysis	Rotary kiln under argon	10-30g	500	0.1	5	? >60min
Research, slow py	Michel et al, 2006	Lab slow pyrolysis	Rotary kiln under argon	10-30g	500	0.1	15	? >60min
RTI Process/ BioTherm Process	Dynamotive, 1999	Fast	Continuous deep FB	Now to 200tpd, but data from ?pilot	472			
Fixed bed	Ryu et al, 2007	Large lab slow pyrolysis	Packed bed in reactor, within furnace.	150-300g (up to 1kg)	400	0.1	10	heat up + 60min
Lab-fast	Mante, 2008	Fast	Bubling FB	Bench - 300-350g/h here	421		fast	
WFPP	Scott et al, 1999	Fast	Continuous shallow FB	5tpd demonstrator, data from ?	500		fast	0.5
Lurgi	Henrich, 2007	Fast	Lurgi-Ruhrgas twin-screw pyrolyser	20kg/h pilot, scaling up to 500kg/h	500	0.1	fast	few seconds
Lurgi	Henrich, 2007	Fast	Lurgi-Ruhrgas twin-screw pyrolyser	20kg/h pilot, scaling up to 500kg/h	500	0.1	fast	few seconds
Haloclean	Hornung, 2008	Intermediate pyrolysis	Rotary kiln, internal screw with steel balls	Pilot 50kg/h, 15t processed	400	0.1	?	2 min
Lab-slow	Zanzi et al, 2003	Lab slow pyrolysis with carbon activation by steam	Vertical tube in furnace - packed bed?	65g	550		25	60min
Haloclean	Hornung et al, 2006	Intermediate pyrolysis	Rotary kiln, internal screw with steel balls	Pilot 50kg/h, 15t processed	400	0.1	?	2 min
Lab-slow	Lievens et al, 2009	Lab slow pyrolysis	Static horrizontal tube with silica heat carrier	3g	350		10	
Lab-slow	Lievens et al, 2009	Lab slow pyrolysis	Static horrizontal tube with silica heat carrier	3g	350		10	
Lab-slow	Zanzi et al, 2002	Lab slow pyrolysis with carbon activation by steam	Vertical tube in furnace - packed bed?	65g	650		25	60min
BEST Energies	Downie et al, 2007	Slow pyrolysis	Drum kiln, agitated	300kg/h dry basis	550+/-30		5-10	

Pyrolysis Process Information: Data Extracted for Selected Feeds														
Reference		Char								Gas				
Process	Source Ref	Yield		Moisture	Volatiles	Fixed-C	Carbon%	Carbon yield	Energy, HHV	Yield		Composition	Energy, HHV	
		%	?basis	%	%	%	%	%	MJ/kg	%	?basis		MJ/kg	MJ/Nm3
Lab-fast	Kim et al, 2009	40.63	%wt			ash				35.88	%wt			
Lab-fast	Mante, 2008	43.1	%wt dry feed							13.6	%wt dry feed			
Lab-fast	Ioannidou et al, 2009	31	%wt as fed (?)			CHO	67.62	20.832	24.27	26	%wt as fed (?)	Vol% CO 51; H 32; CH4 9; CO2 9.	13	
Lab-slow	Ioannidou et al, 2009	37.31	%wt as fed (?)							16.16	%wt as fed (?)	Vol% CO2 51.69; CO 38.21; CH4 4.08; H2 1.82; +C2-C6	8.5	
Lab-fast	Ioannidou et al, 2009	22	%wt as fed (?)			CHO	62.18	13.6796	19.13	45	%wt as fed (?)	Vol% CO 46; H 28; CH4 10; CO2 17.	15	
Lab-slow	Ioannidou et al, 2009	32.67	%wt as fed (?)							14.47	%wt as fed (?)	Vol% CO2 52.36; CO 34.77; CH4 5.49; H2 2.42; +C2-C6	8	
Bio-Alternative	Birdgwater, Peacocke, 2000	30	%wt dry wood		12-18				30			Vol%: H2 7.9; CO 16.3; CO2 13.2; N2 48.4; O and H-C 14.7		3.8-5.5
Pyrovac	Birdgwater, Peacocke, 2000	34	%wt dry wood		20.3	72.1		24.514	30.4	11	%wt dry wood	Vol%: H2 6.6; CH4 10.0; CO 32.0; CO2 41.5; C-2-5 6.4; MeOH 0.4; Others 3.1	10.9	
Lab-slow	Zanzi et al, 2001	24	%wt maf	7.5						10	%wt maf	Vol% N2 free: CO2 52.9; CO 27.9; H2 10; CH4 7.6; C-2 1.6.		
Bioware	Rocha et al, 2002	12-15	%wt dry basis			40-45	52.5	7.0875	20-25	10-12	%wt			
Bioware	Rocha et al, 2002	<10	%wt dry basis			CHON ash	52.5	5.25		15-20	%wt			
Research, slow py	Michel et al, 2006	23	%wt fraction of total						29.083	51	%wt fraction of total	CO2, CO, CH4 not quantified		
Research, slow py	Michel et al, 2006	28	%wt fraction of total							46	%wt fraction of total	CO2, CO, CH4 not quantified		
RTI Process/ BioTherm Process	Dynamotive, 1999	20	%wt as fed							9	%wt as fed			
Fixed bed	Ryu et al, 2007	30	%mass yield		35	63	79.8	23.94	32	34	%mass yield by diff	CO2, CO, CH4, H2, C3H8 not quantified		
Lab-fast	Mante, 2008	22.4	%wt dry feed							14.88	%wt dry feed			
WFPP	Scott et al, 1999	12.2	%wt maf							7.8	%wt maf			
Lurgi	Henrich, 2007	17	?							13	?	CO>CO2>CH4>H2~C2-C5		
Pyrovac	Birdgwater, Peacocke, 2000	24	%wt dry wood							12	%wt dry wood			
Lab - slow	Demirbas, 2001	32.6	?			CHON ash	77	25.102	29.34	20.2	?	na	na	
Lab-fast	Yanik et al, 2007	20	%wt						19 kcal/kg	39	%wt			
RTI Process/ BioTherm Process	Scott et al, 1999	30.2	%wt moisture free feed							21.1	%wt moisture free feed			
RTI Process/ BioTherm Process	Radlein and Kingston, 2007	18	%wt							24	%wt			
WFPP	Scott et al, 1999	24.5	%wt maf							17.8	%wt maf			
Lurgi	Henrich, 2007	28	?							18	?	CO2>CO>CH4>C2-C5>H2		
Haloclean	Hornung, 2008	35	?						25	20	?			
Lab-slow	Zanzi et al, 2003	25	%wt maf	2.5						12	%wt maf	Vol% N2 free: CO2 55.4; CO 21.9; H2 10; CH4 10.9; C-2 1.8.		
Haloclean	Hornung et al, 2006	33.5	?						25	31.9	?			
Lab-slow	Lievens et al, 2009	49.1	%wt as fed							<1				
Lab-slow	Lievens et al, 2009	54	%wt as fed							<1				
Lab-slow	Zanzi et al, 2002	12	%wt maf	2.1						49	%wt maf	Vol% N2 free: CO2 18.5; CO 33.1; H2 43.1; CH4 4.7; C-2 0.6.		
BEST Energies	Downie et al, 2007	40	%wt dry feed			CHNO-Ash	72.3	28.92				Vol%: N2 38; CO 20; CO2 16; H2 16; CH4 8.5; C-2 <1		

Pyrolysis Process Information: Data Extracted for Selected Feeds							
Reference		Liquid					Notes
Process	Source Ref	Oil Yield	Water Yield		Moisture	Energy, HHV	
		%	%	?basis	%	MJ/kg	
Lab-fast	Kim et al, 2009	23.49	included	%wt		27.49	Uncertain yield basis, might be as fed, as liquid yield is just condensates as far as can tell. Mante specifies yields on dry basyis though.
Lab-fast	Mante, 2008	43.25	included	%wt dry feed		29.7	
Lab-fast	Ioannidou et al, 2009	30	included	%wt as fed (?)			Neither of these set-ups seem very representative of large scale fast or slow processes. This 'fast' process seems more like a slow for yield distribution. 520 result picked as 360/380 look anomalous.
Lab-slow	Ioannidou et al, 2009	40.22	included	%wt as fed (?)			Neither of these set-ups seem very representative of large scale fast or slow processes. This 'slow' process has anomalous char yield pattern, highest at 600 (54%). 500 picked as more data given for this.
Lab-fast	Ioannidou et al, 2009	20	included	%wt as fed (?)			Neither of these set-ups seem very representative of large scale fast or slow processes. This 'fast' process seems more like a slow for yield distribution. 520 result picked as 360/380 look anomalous.
Lab-slow	Ioannidou et al, 2009	42.22	included	%wt as fed (?)			Neither of these set-ups seem very representative of large scale fast or slow processes. This 'slow' process has anomalous char yield pattern, highest at 600 (40%). 500 picked as more data given for this.
Bio-Alternative	Birdgwater, Peacocke, 2000	15-20		%wt on feed	4.5	22.2	Gas burnt 'in a boiler' or after drying in an engine. Oil used in a hospital boiler. Char desired product.
Pyrovac	Birdgwater, Peacocke, 2000	35	20	%wt dry wood	23	23	Char burnt for steam -> turbine 5.5MWe; flue gas -> drying; syngas and some biooil -> process heat; biooil -> CC gas turbine 8.5MWe; flue gas -> drying
Lab-slow	Zanzi et al, 2001	66		%wt maf			Yield basis probably % wt mf not maf - otherwise doesn't balance
Bioware	Rocha et al, 2002						
Bioware	Rocha et al, 2002	70-75	inc	%wt			
Research, slow py	Michel et al, 2006	26	included	%wt fraction of total			Char yields higher for slower heating, higher for lower final temp, higher for straw vs pellets - not expected, thin explanation.
Research, slow py	Michel et al, 2006	26	included	%wt fraction of total			Paper gives variation of yields with heating rate and physical form, but data patchy.
RTI Process/ BioTherm Process	Dynamotive, 1999	71		%wt as fed			Data picked from charts, other data for T=459,460,487,505 - good set for variability. Energy data: total heat requirement 2.5MJ/kg, when gases recycled to reactor require 1MJ/kg of external heat input eg nat gas, this at 'six barrels per day plant' scale. No figures for drying requirement. The gas input said to be 5% of 'total CV' of oil yield at max yield.
Fixed bed	Ryu et al, 2007	35	included	%mass yield			Paper gives profiles for yields at five final temperatures, also for GCV, energy yield, char analyses. Data not tabulated - picked off charts so approximate.
Lab-fast	Mante, 2008	62.69	included	%wt dry feed		25.64	
WFPP	Scott et al, 1999	66.5	11.6	%wt maf			
Lurgi	Henrich, 2007	70	included	?			Figures approx, taken off charts, to search for published data
Pyrovac	Birdgwater, Peacocke, 2000	47	17	%wt dry wood			
Lab - slow	Demirbas, 2001	47.2		?			Paper gives good profiles for yields at range of seven final temperatures, but not very representative technique. Five other feeds tested.
Lab-fast	Yanik et al, 2007	35	6	%wt	4.68		
RTI Process/ BioTherm Process	Scott et al, 1999	48.7	?	%wt moisture free feed			Scott paper gives very little data for RTI process, mostly for WFPP comparison. Discussion of RTI mostly on easier design requirements.
RTI Process/ BioTherm Process	Radlein and Kingston, 2007	58		%wt		16.5	
WFPP	Scott et al, 1999	44.7	8.1	%wt maf			Scott, 1985 gives similar data for wheat straw but only as a chart. At 500℃, however, char 35-40%, gas 15-17, total liquid 43-44. Data for two runs.
Lurgi	Henrich, 2007	54	included	?			Figures approx, taken off charts, to search for published data
Haloclean	Hornung, 2008	45	included	?		21	Data in presentations very patchy. Hoping for more detail from Horning, but not arrived yet.
Lab-slow	Zanzi et al, 2003	63		%wt maf			Yield basis probably % wt mf not maf - otherwise doesn't balance
Haloclean	Hornung et al, 2006	34.6	included	?		21	Data in presentations very patchy. Hoping for more detail from Horning, but not arrived yet.
Lab-slow	Lievens et al, 2009	18	22.3	% wt as fed		23-24	Low temp used to keep heavy metals in the char, but possibly not very charred at 350℃. High char yield includes ash, but if expressed on dry higher still - 61, 54.5% wt on dry. Earlier paper has data for higher temps, usual profile of falling yield of char - data on charts.
Lab-slow	Lievens et al, 2009	14.7	19.2	% wt as fed		20-25	Low temp used to keep heavy metals in the char, but possibly not very charred at 350℃. High char yield includes ash, but if expressed on dry higher still - 61, 54.5% wt on dry. Earlier paper has data for higher temps, usual profile of falling yield of char - data on charts.
Lab-slow	Zanzi et al, 2002	39		%wt maf			Yield basis probably % wt mf not maf - otherwise doesn't balance
BEST Energies	Downie et al, 2007	0					No oil product so balance of yield should be gas - 60% by wt. And from carbon analyses given can conclude 37% of C ends up in gas, so should be able to deduce gas quantity and energy from analysis.

References for Appendices 1 and 2

Antal, M.J., Grønli, M. (2003) The art, science and technology of charcoal production. *Industrial and Engineering Chemistry Research.* **42**, (8), 1619-1640.

Antal, M.J., Mochidzuki, K., Paredes, L.S., (2003). Flash carbonisation of biomass. *Industrial and Engineering Chemistry Research.* **42**, 3690-3699.

Badger, P.C., Fransham, P.B. (2006). *Method and system for accomplishing flash or fast pyrolysis with carbonaceous materials.* US Patent Application No.: 11/480915.

BEST Energies Inc. (2009). BEST Energies web site BEST Energies Inc., Wisconsin, USA. http://www.bestenergies.com/companies/bestpyrolysis.html 12.08.09

Bridgwater, A.V., Peacocke, G.V.C. (2000). Fast Pyrolysis Processes for Biomass. *Renewable and Sustainable Energy Reviews.* **4**, 1-73.

Day, D., Evans, R.J., Lee, J.W., Reicosky, D. (2005). Economical CO2, SOx, and NOx capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy.* **30**, 2558-2579.

Demirbas, A. (2001). Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energy Conversion and Management.* **42**, 1229-1238.

Domac, J., Trossero, M., Siemons, R.V. (2008). *Industrial Charcoal Production.* North-West Croatia Regional Energy Agency, Zagreb. http://www.drveniugljen.hr/assets/files/pdf/FAO_Industrial%20charcoal%20production.pdf 15.08.09

Dynamotive Energy Systems Corporation. (1999). BioTherm™ - a system for continuous quality, fast pyrolysis biooil. *Fourth Biomass Conference of the Americas.* http://www.biooil.ru/docs/1999OaklandBiomassPaper.pdf 15.08.09

Henrich, E. (2007). The status of the FZK concept of biomass gasification. *The status of the FZK concept of biomass gasification.* Forschungszentrum Karlsruhe GmbH. Karlsruhe, Germany.

Honsbein, D. (2005). Examples of Biomass Utilisation in South Africa – Application of Slow Pyrolysis *PyNe Newsletter.* **21**, 2-4. http://www.pyne.co.uk/Resources/user/PYNE%20Newsletters/PyNews%2021.pdf 15.08.09

Hornung, A., Apfelbacher, W., Koch, W., Linek, A., Sagi, S., Schoner, J., Stohr, J., Seifert, H., Tumiatti, V., Lenzi, F. (2006). Thermo-chemical conversion of straw - Haloclean intermediate pyrolysis *17th International Symposium on Analytical and Applied Pyrolysis, 2006.*

Hornung, A. (2008). *Fast, intermediate or slow pyrolysis for fuels production, power generation from various biomasses or as pre-conditioning unit for gasifiers.* Presentation to Imperial College. Aston University. Birmingham, UK. http://www3.imperial.ac.uk/pls/portallive/docs/1/44315696.PDF 15.08.09

Ioannidou, O., Zabaniotou, A., Antonakou, E.V., Papazisi, K.M., Lappas, A.A., Athanassiou, C. (2009). Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations. *Renewable and Sustainable Energy Reviews.* **13**, 750-762.

Kammen, D.M., Lew, D.J. (2005). *Review of Technologies for the Production and Use of Charcoal.* National Renewable Energy Laboratory, Golden, Colorado, USA.

Karagoz, S. (2009). Energy production from the pyrolysis of waste biomasses. *International Journal of Energy Research.* **33**, 576-581.

Kim, S.S., Agblevor, F.A., Lim, J. (2009). Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *Journal of Industrial and Engineering Chemistry.* **15**, 247-252.

Lievens, C., Carleer, R., Cornelissen, T., Yperman, J. (2009). Fast pyrolysis of heavy metal contaminated willow: Influence of the plant part. *Fuel.* **88**, 1417-1425.

Mai, R., Liebold, H., Siefert, H. (2008). Hot gas filtration and Haloclean ® process operation experience and scale-up. *7th International Symposium on Gas Cleaning at High Temperatures.* http://www.fzk.de/fzk/groups/itc-tab/documents/internetdokument/id_067802.pdf 15.08.09

Mante, N.O.D. (2008). *Influence of Wood on the Pyrolysis of Poultry Litter.* Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA. http://scholar.lib.vt.edu/theses/available/etd-09082008-120932/unrestricted/Thesis-Pyrolysis.pdf 23.06.09.

Michel, R., Mischler, N., Azambre, B., Finqueneisel, G., Machnikowski, J., Rutowski, P., Zimny, T., Weber, J.V. (2006). Miscanthus × Giganteus straw and pellets as sustainable fuels and raw material for activated carbon. *Environmental Chemistry Letters.* **4**, 185-189.

Okimori, Y., Ogawa, M., Takahashi, F. (2003). Potential of CO2 emission reductions by carbonizing biomass waste from industrial tree plantation in south Sumatra, Indonesia. *Mitigation and Adaptation Strategies for Global Change.* **8**, 261-280.

Piskorz, J., Majerski, P., Radlein, D. (1999). *Energy Efficient Liquefaction of Biomaterials by Thermolysis.* US Patent No.: 5728271.

Pro-Natura. (2008). *Fighting climate change with green charcoal and increasing agricultural productivity.* Newsletter December 2008. Pro-Natura, Paris. http://www.pronatura.org/archives/200812_GreenCharcoal_en.pdf 15.08.09

Radlein, D., Kingston, A. (2007). The Potential role of Agrichar in the Commercialization of Dynamotive's Fast Pyrolysis Process. *International Agrichar Initiative Conference, 2007.* http://www.biochar-international.org/images/Agrichar_May2,_2007_Presentation-Radlein.pdf 15.08.09

Rocha, J.D., Olivares Gómez, E., Mesa Pérez, J.M., Cortez, L.A.B., Seye, O., Brossard González, L.E. (2002). The demonstration fast pyrolysis plant to biomass conversion in Brazil. *World Renewable Energy Congress VII.*

Ryu, C., Sharifi, C.N., Swithenbank, J. (2007). Waste pyrolysis and generation of storable char. *International Journal of Energy Research.* **31**, 177-191.

Scott, D.S., Piskorz, J., Radlein, D. (1985). Liquid Products from the Continuous Flash Pyrolysis of Biomass. *Industrial and Engineering Chemistry Process Design and Development.* **24**, 581-588.

Scott, D.S., Majerski, P., Piskorz, J., Radlein, D. (1999). A second look at fast pyrolysis of biomass - the RTI process. *Journal of Analytical and Applied Pyrolysis.* **51**, 23-37.

Sea Marconi. (2009). *Haloclean BioEnergy - Principles of Operation.* Sea Marconi web site. http://www.seamarconi.com/modules.php?name=News&file=article&sid=139 15.08.09

Someus, G.E. (1993). *Method and apparatus for refinement of organic material.* US Patent No.: 5194069.

Toole, A.W., Lane, P.H., Arbogast, C., Smith, W.R., Peter, R., Locke, E.G., Beglinger, E, Erickson, E.C.O. (1961). *Charcoal Production, Marketing and Use.* Forest Service, US Department of Agriculture. Report No.: 2213 http://www.fpl.fs.fed.us/documnts/fplr/fplr2213.pdf 15.08.09

Yanik, J., Kornmayer, C., Saglam, M., Yuksel, M. (2007). Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. *Fuel Processing Technology.* **88**, 942-947.

Yeboah, Y.D., Bota, K.B., Wang, Z., Gronich, S., Evans, R. (2003). *Hydrogen from Biomass for Urban Transportation.* FY 2003 Progress Report. National Renewable Energy Laboratory, Golden, Colorado, USA. http://www.hydrogen.energy.gov/pdfs/progress04/va3_yeboah.pdf 15.08.09

Zabaniotou, A.A., Karabelas, A.J. (1999). The Evritania (Greece) demonstration plant of biomass pyrolysis. *Biomass and Bioenergy.* **16**, 431-445.

Zanzi, R., Bai, X., Capdevila, P., Bjornbom, E. (2001). Pyrolysis of biomass in the presence of steam for preparation of activated carbon, liquid and gaseous products. *6th World Congress of Chemical Engineering, 2001.*

APPENDIX 3

Pyrolysis Process Model

The following page holds a print of one sheet from the spreadsheet model. Each model case has a similar sheet; the one shown here is the default model case with arbitrary input data.

Copies of the spreadsheet may be available from the author or Dr Ondřej Masek, UKBRC, University of Edinburgh.

Simple Carbon Balance Model

Case Sheet: Model

The model sheet is protected

Data input areas in BLUE
Transferred data in YELLOW (in or out of model)
Output data in GREEN
Balances to adjust in PINK
Currently assuming dry biomass input - not handled drying yet
Also not considering use of waste heat - but this could be for drying

Model Inputs

Process Input			
Biomass	kg dry feed	1	default
Carbon content	%	50	default
Energy value	MJ/kg	19	default
Pyrolysis Process			
Mass Yield			
Gas	%	30	
Liquid	%	30	
Char	%	40	
Energy loss	%	7.894737	to balance could alter output HVs instead
Process energy	% input	10	default
Primary Process Output			
Gas			
Energy value	MJ/kg	10	default
Carbon content	%	30	default
Liquid			
Energy value	MJ/kg	15	default
Carbon content	%	35	default
Char			
Energy value	MJ/kg	25	default
Carbon content	%	75	default
Product Conversion			
Gas			
Recycled	%	63.33333	to balance could alter process req instead
Energy conversion	%	33	default
Liquid			
Recycled	%	0	
Energy conversion	%	33	default
Char			
Recycled	%	0	
Converted	%	0	
Energy conversion	%	33	default
Biomass Combustion			
Energy conversion	%	33	
Waste Heat			
Heat conversion	%	40	

Process Input		
Biomass	kg	1
Carbon content	%	50
Carbon	kg	0.5
Energy value	MJ/kg	19
Energy	MJ	19

Pyrolysis Process		
Mass Yield		
Gas	%	30
Liquid	%	30
Char	%	40
Energy loss	%	7.8947
Energy loss	MJ	1.5
Process energy	% input	10
Process energy	MJ	1.9

Balances	%
Mass	100
Energy	100.00
Carbon	99.00
Process recycle	100.00

Combustion comparison		
Carbon out	kg	0.5
CO2 out	kg	1.8333
Energy conversion	%	33
Energy product	MJ	6.27
Energy product	kWhe	1.7417

Primary Process Output		
Gas	kg	0.3
Energy value	MJ/kg	10
Energy	MJ	3
Carbon content	%	30
Carbon	kg	0.09
Liquid	kg	0.3
Energy value	MJ/kg	15
Energy	MJ	4.5
Carbon content	%	35
Carbon	kg	0.105
Char	kg	0.4
Energy value	MJ/kg	25
Energy	MJ	10
Carbon content	%	75
Carbon	kg	0.3

Available Heat Estimate		
Heat conversion	%	40
Heat product	MJ	2.24
Heat product	kWht	0.62
Would vaporize	kg water	0.99

Product Conversion		
Gas		
Recycled	%	63.33333
Converted	%	36.66667
Energy conversion	%	33
Energy product	MJ	0.36
Energy product	kWhe	0.10
CO2 out	kg	0.33
Liquid		
Recycled	%	0
Converted	%	100
Energy conversion	%	33
Energy product	MJ	1.49
Energy product	kWhe	0.41
CO2 out	kg	0.39
Char		
Recycled	%	0
Converted	%	0
Retained	%	100
Energy conversion	%	33
Energy product	MJ	0.00
Energy product	kWhe	0.00
CO2 out	kg	0
CO2 in char	kg	1.1
Pyrolysis Product Conversion totals		
CO2 out	kg	0.72
Energy product	MJ	1.85
Energy product	kWhe	0.51

CO2 Balance	Sink	Release
	kg	kg
Pyrolysis		
In biomass	-1.8333333	
Product conversion		0.72
EITHER		
Nat. Gas subst		-0.1037
Sub-tot	-1.8333333	0.61
OR Coal subst		-0.1784
Sub-tot	-1.8333333	0.5366
OR UK Grid Marginal CEF		-0.221
Sub-tot	-1.8333333	0.49
Combustion		
In biomass	-1.8333333	
Combustion		1.833333
Nat. Gas subst		-0.3518
Sub-tot	-1.8333333	1.481568
OR Coal subst		-0.6053
Sub-tot	-1.8333333	1.2280
OR UK Grid Marginal CEF		-0.749
Sub-tot	-1.8333333	1.084

Net CO2 benefit
which includes the char sink and the fossil fuels offset

	Method 1	Method 2
Pyrolysis		
	kg	kg
Nat. Gas subst	-0.1037	
Sub-tot	-1.22	-1.20
OR Coal subst	-0.1784	
Sub-tot	-1.30	-1.28
OR UK Grid Marginal CEF	-0.221	
Sub-tot	-1.34	-1.32
	Char-C CO2e	
	kg/kg dry feed	
In biomass	1.10	
Combustion		
Method 1 or 2		
kg		
Nat. Gas subst	-0.35	
OR Coal subst	-0.6053	
Sub-tot	-0.61	
OR UK Grid Marginal CEF	-0.749	
Sub-tot	-0.75	

**Sum of CO2 in char and fossil fuels offset (both negative) may not quite balance with net CO2 benefit if carbon balance not exact

Char stability factor: 1
(Modifies cell T33 - CO2 in char)

Model Outputs

Pyrolysis Product Conversion totals		
CO2 out	kg	0.72
Energy product	MJ	1.85
Energy product	kWhe	0.51
Char-C CO2e	kg/kgdf	1.10
Enery /Char-C	kWhe/kg-C	1.71 **

Net CO2 benefit		Method 1 kg/kgdf	Method 2 kg/kgdf	Ratio
Pyrolysis	Nat Gas	-1.22	-1.20	1.015231
	Coal	-1.30	-1.28	1.014341
	UK Grid	-1.34	-1.32	
Combustion	Nat Gas	-0.35	-0.35	
	Coal	-0.61	-0.61	
	UK Grid	-0.75	-0.75	

Relative CO2 Benefit			
Kg CO2e / kWh	Substituting		
Pyrolysis	Nat Gas	-2.38	-2.34
	Coal	-2.53	-2.49
	UK Grid	-2.61	-2.57
Combustion	Nat Gas	-0.20	-0.20
	Coal	-0.35	-0.35
	UK Grid	-0.43	-0.43

Available heat		
Heat product	MJ	2.24
Heat product	kWht	0.62

Overall efficiency		
Feed consumption	kgdf/kWhe	1.95
As electricity	%	9.73
As heat	%	11.79
Combined	%	21.52

To use:
Decide on input data, process data, primary product data and enter this
Then look at energy, carbon balances and process recycle and balance these up to near 100
Can use >Tools>Goal Seaker to balance to 100
Chose if any char to be converted to power

Waste heat estimate added to check enough available to dry biomass.

Comments on default model:
The values put in as defaults are estimated as typical for a 'good' slow pyrolysis.
The carbon has not been balanced as close enough with round numbers.
The energy loss has been fitted to balance - I use a 10% default in other cases.
The gas recycle has been fitted to balance.
The output values are better than those of real slow-py cases.

**added this calc later

Methods converge when the carbon balance is perfect
Deviation in energy or recycle balances affect value, but not convergence

This isn't what you actually emit, it's the offset, which is the only benefit here, so its right that it is the same as the source data

Inputs in this area are not changed from case to case

Fossil fuels substitution		Pyrolysis kg	GWP	CO2e kgCO2e	Combustion kg	GWP	CO2e kgCO2e
Nat Gas							
CO2	kg/GJ	56	0.103	1	0.1035	0.35112	1	0.3511
CH4	kg/GJ	0.001	0.000	72	0.0001	6.27E-06	72	0.0005
N20	kg/GJ	0.0001	0.000	310	0.0001	6.27E-07	310	0.0002
		Totals			0.1037			0.3518
Coal								
CO2	kg/GJ	96	0.177	1	0.1774	0.60192	1	0.6019
CH4	kg/GJ	0.001	0.000	72	0.0001	6.27E-06	72	0.0005
N20	kg/GJ	0.0015	0.000	310	0.0009	9.405E-06	310	0.0029
		Totals			0.1784			0.6053

IPCC Data from G&L paper

UK Grid Marginal CO2 emission factor, DEFRA guidance			
	Pyrolysis kgCO2e	Combustion kgCO2e	/kgdf
kgCO2e/kWhe	0.43	0.221	0.749
kgCO2e/GJ	119	0.221	0.749